

VOLUME 36

NOVEMBER 1958

NUMBER 11

Canadian Journal of Chemistry

Editor: LÉO MARION

Associate Editors:

HERBERT C. BROWN, *Purdue University*
A. R. GORDON, *University of Toronto*
C. B. PURVES, *McGill University*
Sir ERIC RIDEAL, *Imperial College, University of London*
J. W. T. SPINKS, *University of Saskatchewan*
E. W. R. STEACIE, *National Research Council of Canada*
H. G. THODE, *McMaster University*
A. E. VAN ARKEL, *University of Leiden*

Published by THE NATIONAL RESEARCH COUNCIL

OTTAWA

CANADA

CANADIAN JOURNAL OF CHEMISTRY

(Formerly Section B, Canadian Journal of Research)

Under the authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research, the National Research Council issues THE CANADIAN JOURNAL OF CHEMISTRY and five other journals devoted to the publication, in English or French, of the results of original scientific research. Matters of general policy concerning these journals are the responsibility of a joint Editorial Board consisting of: members representing the National Research Council of Canada; the Editors of the Journals; and members representing the Royal Society of Canada and four other scientific societies.

The Chemical Institute of Canada has chosen the Canadian Journal of Chemistry as its medium of publication for scientific papers.

EDITORIAL BOARD

Representatives of the National Research Council

A. Gauthier, *University of Montreal*
R. B. Miller, *University of Alberta*

H. G. Thode, *McMaster University*
D. L. Thomson, *McGill University*

Editors of the Journals

D. L. Bailey, *University of Toronto*
T. W. M. Cameron, *Macdonald College*
H. E. Duckworth, *McMaster University*

K. A. C. Elliott, *Montreal Neurological Institute*
Léo Marion, *National Research Council*
R. G. E. Murray, *University of Western Ontario*

Representatives of Societies

D. L. Bailey, *University of Toronto*
Royal Society of Canada
T. W. M. Cameron, *Macdonald College*
Royal Society of Canada
H. E. Duckworth, *McMaster University*
Royal Society of Canada
Canadian Association of Physicists

K. A. C. Elliott, *Montreal Neurological Institute*
Canadian Physiological Society
P. R. Gendron, *University of Ottawa*
Chemical Institute of Canada
R. G. E. Murray, *University of Western Ontario*
Canadian Society of Microbiologists

T. Thorvaldson, *University of Saskatchewan*, Royal Society of Canada

Ex officio

Léo Marion (Editor-in-Chief), *National Research Council*
J. B. Marshall (Administration and Awards), *National Research Council*

Manuscripts for publication should be submitted to Dr. Léo Marion, Editor-in-Chief, Canadian Journal of Chemistry, National Research Council, Ottawa 2, Canada.

(For instructions on preparation of copy, see *Notes to Contributors* (inside back cover).)

Proof, correspondence concerning proof, and orders for reprints should be sent to the Manager, Editorial Office (Research Journals), Division of Administration and Awards, National Research Council, Ottawa 2, Canada.

Subscriptions, renewals, requests for single or back numbers, and all remittances should be sent to Division of Administration and Awards, National Research Council, Ottawa 2, Canada. Remittances should be made payable to the Receiver General of Canada, credit National Research Council.

The journals published, frequency of publication, and prices are:

| | | |
|-------------------------------------------------|-----------|---------------|
| Canadian Journal of Biochemistry and Physiology | Monthly | \$3.00 a year |
| Canadian Journal of Botany | Bimonthly | \$4.00 a year |
| Canadian Journal of Chemistry | Monthly | \$5.00 a year |
| Canadian Journal of Microbiology | Bimonthly | \$3.00 a year |
| Canadian Journal of Physics | Monthly | \$4.00 a year |
| Canadian Journal of Zoology | Bimonthly | \$3.00 a year |

The price of regular single numbers of all journals is 75 cents.

Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 36

NOVEMBER 1958

NUMBER 11

FUSED HETEROCYCLICS

PART II. SYNTHESIS OF QUINOLINO-(2:3:3':2')-QUINOLINE: AN ISOMER OF CALYCANINE^{1,2}

RAGINI ANET³

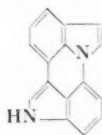
ABSTRACT

The constitution of calycanine, a dehydrogenation product of the alkaloid calycanthine, is discussed. Calycanine dipicrate has been prepared, and, on the basis of its analysis and the infrared spectrum of calycanine, a quinolinoquinoline structure has been put forward for calycanine. The synthesis of quinolino-(2:3:3':2')-quinoline is described.

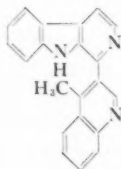
Calycanine is an important degradation product of the alkaloid calycanthine (1). At the time that this work was carried out, the constitution of calycanine was not known,⁴ and it was decided to investigate this base as a part of the studies on calycanthine (2).

Calycanine was first prepared by Marion and Manske (4) by the selenium dehydrogenation of the alkaloid, and later by Barger, Madaniveitia, and Streuli (5) by heating calycanthine with a variety of reagents. Calycanine, m.p. 310° C after sublimation, was found to be a very stable weak base, giving faintly fluorescent solutions. It did not give any coloration with *p*-dimethylaminobenzaldehyde (Ehrlich reaction). Elementary analysis led both groups of workers to put forward a $C_{16}H_{10}N_2$ formula for calycanine. One active hydrogen and no N-methyl group was found.

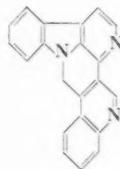
Barger *et al.* (5), on the basis of their formula for calycanthine, put forward structure (I) for calycanine. Manske and Marion (6) considered that Barger's structure was inconsistent with the properties of calycanine, viz., the negative Ehrlich reaction and its basicity. As a result of further analyses of the base they proposed a $C_{21}H_{16}N_3$ or $C_{21}H_{13}N_3$ formula for calycanine, and the structures (II) or (IIa).



(I)



(II)



(IIa)

¹Manuscript received July 23, 1958.

Contribution from the Dyson-Perrins Laboratory, Oxford.

²Somasekhara, S. and Phadké, R. *J. Indian Inst. Sci. A*, **37**, 120 (1955) forms Part I.

³nee Phadké. Present address: c/o Dr. F. A. L. Anet, Department of Chemistry, University of Ottawa.

⁴This work was recorded in a part of a D. Phil. Thesis, Oxford University, 1952. After the completion of this work, we became aware of the unpublished work of Clark and Woodward at Harvard University, who synthesized quinolino-(3:4:4':3')-quinoline and found it to be identical with calycanine (3).

At this stage, Hargreaves reported an X-ray investigation of calycanine (7). Although the results were not conclusive, he suggested that the size of the unit cell favored a C_{16} formula and that the molecule of calycanine was centrosymmetrical (8). Later, Manske, Marion, and Kulka (9) synthesized 2-(3-lepidyl)-3-carboline (II) and found it to be different from calycanine. They discarded the C_{21} expression and proposed a $C_{15}H_{10}N_2$ formula as being in agreement with their analytical figures and with the molecular weight according to Hargreaves's data.

In the present investigation, calycanine was prepared according to Barger *et al.* (5) by the zinc dust distillation of calycanthine. Analysis of the base did not distinguish between a C_{15} and a C_{16} formula, but calycanine formed a *dipicrate* whose analysis was in better agreement with the C_{16} than with the C_{15} formula. The infrared spectrum of calycanine showed no band attributable to an $-NH$ group, thus ruling out both Barger's structure (I) and an indoloquinoline or indoloisoquinoline structure as suggested by the Canadian workers (9). The active hydrogen in calycanine must therefore be contained in a structural feature other than an $-NH$ group. A quinolinoquinoline system in which the two pyridine rings are fused together, would, it was felt, fulfill such a requirement. Furthermore, such a system could easily arise from two indole nuclei as follows.

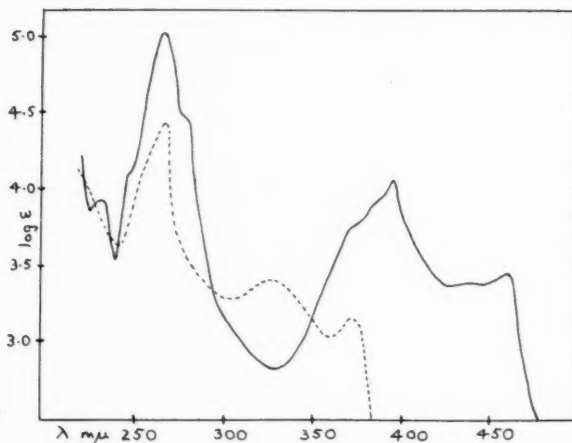
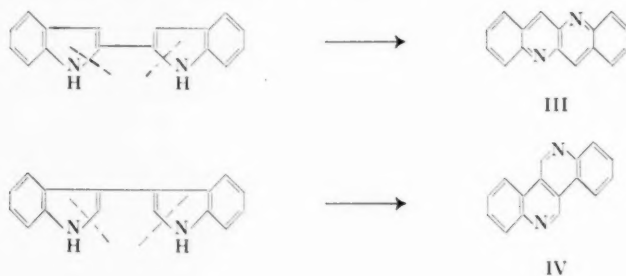


FIG. 1. Ultraviolet absorption spectra in methanol.
 - - - Calycanine
 — Quinolino-(2:3:3':2')-quinoline

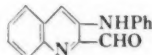
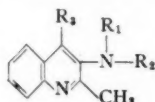
Of the six quinolinoquinoline structures formed by the fusion of the two pyridine nuclei, only two, quinolino-(2:3:3':2')-quinoline (III) and quinolino-(3:4:4':3')-quinoline, are centrosymmetrical. We have now synthesized the former, and found it to be different from calycanine. By exclusion of alternatives, structure (IV) was proposed for calycanine (cf. 2).

A possible explanation for the active hydrogen found in the Zerewitinoff determination on calycanine may be that one mole of the Grignard reagent adds to the C=N linkage of one quinoline ring, and as a result, the hydrogen atom on the carbon γ to the nitrogen of the other quinoline ring is activated.

The ultraviolet absorption spectrum of calycanine is recorded in Fig. 1.

Synthesis of Quinolino-(2:3:3':2')-quinoline: Epindoline

Although the base itself has not been prepared previously, two of its derivatives, viz., 4:4'-dihydroxy-6:6'-dimethyl- (10) and 4:4'-dihydroxyquinolino-(2:3:3':2')-quinoline (11), have been synthesized. The hydroxyl groups in the quinolinoquinoline or epindoline (10) system were found to be resistant to reduction (10) or acylation (11). The synthesis of the unsubstituted base was carried out as follows.



X

| | |
|------------------------------|-----------------|
| V. $R_1 = R_2 = H$; | $R_3 = COOH$ |
| VI. $R_1 = Ph$; $R_2 = H$; | $R_3 = COOH$ |
| VII. $R_1 = R_2 = Ph$; | $R_3 = COOH$ |
| VIII. $R_1 = Ph$; | $R_2 = R_3 = H$ |
| IX. $R_1 = R_2 = Ph$; | $R_3 = H$ |

When 3-aminoquinaldine-4-carboxylic acid (V) (12) was heated with iodobenzene and copper catalyst under conditions described for the conversion of anthranilic acid to *o*-phenylaminobenzoic acid (13), a mixture of 3-phenylamino- and 3-diphenylamino-quinaldine-4-carboxylic acids (VI and VII respectively) was obtained. Attempts to prepare the monosubstituted acid exclusively were unsuccessful. It may be noted that 3-aminoquinaldine could not be arylated directly to give 3-arylaminquinaldine (12, 14) and we have confirmed this difficulty in the reaction of 3-aminoquinaldine with iodobenzene. The mixture of carboxylic acids (VI and VII) could not be separated very satisfactorily, but the mixture of 3-phenylamino- and 3-diphenylamino-quinaldines (VIII and IX respectively) obtained on decarboxylation of the acids could be easily separated by chromatography over alumina.

Oxidation of 3-phenylaminoquinaldine with selenium dioxide, a reagent previously used for the oxidation of quinaldine to quinoline-2-aldehyde (15), gave 3-phenylaminoquinoline-2-aldehyde in 50% yield. It is interesting that this oxidation took place smoothly in spite of the presence of an easily oxidizable phenylamino group. Cyclization of the aldehyde to quinolino-(2:3:3':2')-quinoline was successful with concentrated sulphuric acid at 100° C, under the milder conditions described for the cyclization of *o*-phenylaminobenzaldehyde (13), the aldehyde (X) was recovered unchanged. The epindoline (III) was a bright yellow compound which charred but did not melt at 280° C. Its solutions in organic solvents were strongly fluorescent. The ultraviolet absorption spectrum of (III) is recorded in Fig. 1.

EXPERIMENTAL

All melting points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

Calycanine

This was prepared essentially according to Barger *et al.* (5) by the zinc dust distillation of calycanthine. At the same time, a neutral fraction smelling strongly of indole was obtained, but it failed to give any crystalline products. The basic portion gave calycanine, m.p. 302°–305° C, which was repeatedly sublimed to give needles from methanol, m.p. 306°–307° C. Its solution in methanol was faintly fluorescent in ultraviolet light, the fluorescence was unchanged on addition of alkali, but was slightly depressed with mineral acid. Found: C, 82.9; H, 4.4. Calc. for $C_{16}H_{10}N_2$: C, 83.5; H, 4.4%. Calc. for $C_{15}H_{10}N_2$: C, 82.5; H, 4.6%.

Calycanine Dipicrate

Chloroform solutions of calycanine and picric acid were heated together for a few minutes. On cooling, calycanine dipicrate separated as needles. It dissociated rapidly in alcohol and water but could be crystallized from chloroform containing picric acid in red needles, m.p. 238°–239° C. Found: C, 48.7; H, 2.39. Calc. for $C_{16}H_{10}N_2 \cdot 2C_6H_3N_3O_7$: C, 48.8; H, 2.32. Calc. for $C_{15}H_{10}N_2 \cdot 2C_6H_3N_3O_7$: C, 47.9; H, 2.36%.

3-Phenylaminoquinaldine-4-carboxylic Acid (VI)

Three grams of 3-aminoquinaldine-4-carboxylic acid (V) (12), 3.3 ml iodobenzene, 4.7 g freshly dried anhydrous potassium carbonate, and 0.15 g Ullmann's copper catalyst (Naturkupfer C) were refluxed in a mixture of 20 ml cyclohexanol and 20 ml benzyl alcohol for 2 hours with strict exclusion of moisture. The reaction mixture was diluted with 50 ml water and steam-distilled to remove the alcohols. The solution was filtered hot and poured into dilute acetic acid. After 6–8 hours at room temperature, the flocculent precipitate was filtered (3.1 g, m.p. 250°–268° C) and extracted with a 1:1 mixture of chloroform-methanol to remove the disubstituted acid as well as some unchanged 3-amino acid. The residue (1.8 g) was crystallized from ethanol containing some pyridine in rhomboid needles, m.p. 298°–300° C with decomposition. Found: C, 73.0; H, 5.0. Calc. for $C_{17}H_{14}N_2O_2$: C, 73.4; H, 5.4%. The acid was sparingly soluble in alcohol, ether, benzene, and chloroform but easily soluble in pyridine. It did not dissolve readily in either dilute or concentrated hydrochloric acid, but gave a colorless potassium salt.

3-Phenylaminoquinaldine (VIII)

Two grams of the above acid (VI) was heated at 290°–300° C for 30 minutes. The acid melted with decomposition and some of the base sublimed into the condenser attached to the reaction flask. The melt was allowed to cool and extracted with methanolic hydrochloric acid. The acid extract was filtered, diluted with 50 ml water, and made strongly alkaline with potassium hydroxide. Ether extraction of the aqueous solution (charcoal) gave an oil which solidified on refrigeration (1.8 g, m.p. 90°–111° C). The base (VIII) was crystallized from very dilute alcohol in needles, m.p. 120°–121° C (lit. (16), m.p. 120°–121° C). Found: C, 82.1; H, 5.7. Calc. for $C_{16}H_{14}N_2$: C, 82.0; H, 6.0%. The base was very soluble in organic solvents to give non-fluorescent solutions.

The *picrate* formed in ethanol crystallized from the same solvent in golden yellow prisms, m.p. 230° C with decomposition. Found: C, 57.1; H, 3.8. Calc. for $C_{16}H_{14}N_2 \cdot 2C_6H_3N_3O_7$: C, 57.0; H, 3.7%.

3-Diphenylaminoquinaldine-4-carboxylic Acid (VII)

The chloroform-methanol extract from the preparation of the 3-phenylamino acid (VI) was evaporated to dryness and the residue repeatedly crystallized from the same solvents in stout needles, m.p. 270°–273° C with decomposition. Found: N, 7.6. Calc. for $C_{23}H_{18}N_2O_2$: N, 7.9%. The acid was soluble in chloroform and acetic acid, less so in acetone, and sparingly soluble in cold alcohol and benzene.

3-Diphenylaminoquinaldine (IX)

The diphenylamino acid (VII, 0.5 g) was decarboxylated by heating at 270°–275° C for 20 minutes. On working up the reaction mixture, as in the case of 3-phenylaminoquinaldine (VIII), the base was obtained as a yellow oil which solidified on trituration with alcohol. Crystallization from aqueous ethanol gave colorless prisms, m.p. 141°–142° C. Found: N, 9.2. Calc. for $C_{22}H_{18}N_2$: N, 9.0%. The base dissolved easily in organic solvents to give solutions with a vivid blue fluorescence.

The *picrate* prepared in ethanol formed yellow needles, m.p. 222°–223° C. Found: N, 12.8. Calc. for $C_{22}H_{18}N_2 \cdot C_6H_3N_3O_7$: N, 12.9%.

3-Phenylaminoquinoline-2-aldehyde (X)

3-Phenylaminoquinaldine (VIII, 0.9 g) and 0.45 g freshly prepared selenium dioxide were refluxed in 10 ml purified dioxan containing 1–2 drops of water. A vigorous reaction set in after 2 minutes and the solution turned dark, forming a red deposit of selenium. The heating was discontinued until the initial reaction was over, and the solution refluxed for a further 90 minutes. The dioxan was removed under reduced pressure and the black residue extracted with hot benzene (charcoal). Evaporation of the benzene extract gave an orange oil which solidified with a little cold ethanol (0.5 g, m.p. 98°–104° C). It was crystallized from dilute ethanol in needles, m.p. 109°–110° C. Found: C, 77.0; H, 4.8. Calc. for $C_{16}H_{12}N_2O$: C, 77.4; H, 4.8%. The aldehyde was very soluble in ether, benzene, and chloroform. An ethanolic solution of the aldehyde gave a deep red color with 2:4-dinitrophenylhydrazine hydrochloride in ethanol.

The *phenylhydrazone* was prepared by mixing an alcoholic solution of the aldehyde with a solution of phenylhydrazine in 50% acetic acid. On standing at room temperature for 1 hour, the phenylhydrazone separated as a red solid crystallizing from alcohol in yellow needles, m.p. 221–222° C. Found: C, 77.3; H, 5.4. Calc. for $C_{22}H_{18}N_4$: C, 77.9; H, 5.3%.

Quinolino-(2:3:3':2')-quinoline: Epindoline (III)

The aldehyde (X, 0.37 g) was heated with 1.4 ml concentrated sulphuric acid at 100° C under anhydrous conditions for 1 hour. The initial addition of sulphuric acid dissolved the aldehyde with evolution of heat. At the end of the reaction, the solution was poured into ice-cold water and made alkaline with ammonia. The precipitated solid (0.15 g) was extracted with 100 ml chloroform. Evaporation of chloroform gave bright yellow feathery needles, which were washed with ether to remove uncyclized aldehyde and crystallized from xylene to give stout yellow rods of epindoline which charred but did not melt at 280° C. Found: C, 83.2; H, 4.7. Calc. for $C_{16}H_{10}N_2$: C, 83.5; H, 4.4%. The base was sparingly soluble in ether, but moderately so in benzene, chloroform, and ethyl acetate. Its solutions in these solvents were bright yellow and gave a vivid green fluorescence on addition of a trace of ethanol. The solutions turned orangish and the fluorescence disappeared on addition of hydrochloric acid.

The *picrate* formed in chloroform gave red needles from alcohol containing picric acid, and melted at 308°–310° C with decomposition. Found: C, 57.3; H, 2.8. Calc. for $C_{16}H_{10}N_2 \cdot C_6H_3N_3O_7$: C, 57.5; H, 3.0%.

ACKNOWLEDGMENTS

The author is indebted to Sir Robert Robinson, O.M., F.R.S., for his advice and encouragement, and to the University of Bombay for a Sir Mangaldas Nathubhai Scholarship.

REFERENCES

1. HENRY, T. A. The plant alkaloids. J. & A. Churchill, Ltd., London. 1949. p. 485.
2. ROBINSON, R. and TEUBER, H. J. Chem. & Ind. 783 (1954).
3. SAXTON, J. E. Quart. Revs. (London), **10**, 119 (1956).
4. MARION, L. and MANSKE, R. H. F. Can. J. Research, B, **16**, 432 (1938).
5. BARGER, G., MADANIVEITIA, J., and STREULI, P. J. Chem. Soc. 510 (1939).
6. MANSKE, R. H. F. and MARION, L. Can. J. Research, B, **17**, 293 (1938).
7. HARGREAVES, A. Nature, **152**, 600 (1943).
8. HARGREAVES, A. and TAYLOR, W. H. J. Sci. Instr. **18**, 138 (1941).
9. MANSKE, R. H. F., MARION, L., and KULKA, M. Can. J. Research, B, **24**, 224 (1946).
10. AINLEY, A. D. and ROBINSON, R. J. Chem. Soc. 1508 (1934).
11. DIESBACH, H. DE, SCHURCH, A., and CAVIN, G. Helv. Chim. Acta, **31**, 716 (1948).
12. LAWSON, W., PERKIN, W. H., Jr., and ROBINSON, R. J. Chem. Soc. 635 (1924).
13. ALBERT, A. The acridines. Edward Arnold & Co., London. 1951.
14. CLEMO, G. R. and SWAN, G. A. J. Chem. Soc. 867 (1945).
15. KAPLAN, H. J. Am. Chem. Soc. **63**, 2654 (1941).
16. BRIT. PAT. No. 448,502. Chem. Abstr. **30**, 7588 (1936). U.S. Pat. 2,098,927. Chem. Abstr. **32**, 193 (1938).

ELECTROLYSIS OF LITHIUM HYDRIDE¹

M. A. WEINBERGER, T. J. MOUSSEAU,² AND O. MAASS³

ABSTRACT

A method has been developed whereby current yields of as high as 70% of anodically discharged hydrogen can be maintained during continuous electrolysis of lithium hydride at or just below its melting point. Efforts to utilize this process for the separation of hydrogen and deuterium were unsuccessful.

INTRODUCTION

The electrolysis of heated lithium hydride was first investigated by Moers (1), who described a number of disturbing side effects which dogged his experiments. These showed up as wild fluctuations on the electrical meters monitoring the electrolysis and were ascribed by him to formation of lithium whiskers or metal fog which shorted the electrodes. This work was followed by that of Peters (2), who was able to demonstrate the validity of Faraday's laws for the separation of the electrolysis products. Optimum current efficiencies* for the electrolysis were found using solid lithium hydride at temperatures between 550 and 630° C, currents of 1-3 amp and electrolysis times of up to 3 minutes. In these experiments the hydrogen was pumped off as it was formed and corrections were made for hydrogen produced by thermal decomposition. Above the melting point, hydrogen evolution by electrolysis was found to be irregular and zero current yields were sometimes obtained. Other experiments showed that current yields dropped with increasing electrolysis times. Finally, Potter and Bockris (3) carried out electrolyses under hydrogen pressures of 1 atm to suppress thermal dissociation and showed that the electrolytically separated hydrogen was actually of anodic origin only. These workers also found that good current efficiencies (above 80%) were only obtained by electrolyzing for short times (up to 2½ minutes) at temperatures below the melting point (570-610° C). One-half minute electrolysis at 680° C gave 27% yield, while a prolonged electrolysis (17.5 minutes) at 635° C gave only 2% of the amount of hydrogen calculated by Faraday's law. Recombination of the electrolysis products was believed to be the reason for the low efficiencies.

It appears that the liberated lithium metal is principally responsible for low electrolytic hydrogen yields and most of the apparent anomalies during the electrolyses. In the present work it was attempted to overcome this by depositing the lithium at a cathode with which it would form an alloy. Lithium alloys have been produced by electrolyzing fused lithium chloride-potassium chloride mixtures using the molten alloying metal as cathode (4). If lithium metal could in this way be prevented from spreading into or floating on the hydride and thus kept away from the hydrogen liberated at the anode, better yields should be obtainable. The choice of lithium scavenger cathode was limited to metals having a melting point below that of lithium hydride. Lead and aluminum were chosen. It was realized that because of their ability to form alloys with lithium these metals might decompose lithium hydride themselves, but it was hoped that some kind of equilibrium would be reached.

¹Manuscript received August 8, 1958.

Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Issued as D.R.C.L. Report No. 281.

²Present address: Dominion Observatory, Seismology Division, Ottawa.

³National Research Council, Ottawa.

*The current efficiency or yield is $\frac{\text{amount of product formed} \times 100\%}{\text{theoretical amount from Faraday's laws}} = \frac{\text{cc of hydrogen at n.t.p.}}{.0696 \times \text{amp minute}} \%$.

EXPERIMENTAL

The principal features of the electrolysis cell design were determined by the requirement that lithium deposition should occur only at the scavenger cathode. In addition, because of the corrosive nature of lithium hydride, possible cell materials were restricted to Armco iron or certain stainless steels (5), and no ceramic insulating materials could be used. The scavenger cathode then being in contact with the metallic cell walls, the latter had to be insulated from the active electrolyte to prevent lithium deposition there. This could be achieved by utilizing the poor electrical conductivity of solid lithium hydride at more than 150° below its melting point. Accordingly the cell was heated in such a way as to provide fused or nearly fused electrolyte between anode and scavenger cathode while at the same time maintaining an insulating layer of cooler solid lithium hydride on the walls of the cell not covered by the scavenger. The main heat input was therefore into the molten cathode and into the internally heated anode. By means of thermocouples, temperatures were measured in the cathode pool and at various points along the cell wall but could not be measured in the active electrolyte as the presence of metal there would have provided an auxiliary electrode.

The apparatus is shown in Fig. 1. The anode was supported by the cell lid from which it was electrically insulated and a means was provided to move it up or down in the cell. The lid and the upper part of the cell were water-cooled to protect the vacuum sealing gaskets and in addition a tube passing down the hollow anode shaft played cool nitrogen on the shaft wall opposite the teflon gasket. The temperatures of any of the gaskets never rose much above room temperature.

A conventional vacuum and gas handling system was attached to the cell.

The cell, lid, and anode were fabricated from 347 stainless steel, one of the materials recommended for use with lithium hydride (5). This material was chosen as it has a lower hydrogen permeability than pure iron. Welding was kept to a minimum and was done by the inert gas arc process. The cell after prolonged evacuation was first treated with hydrogen at 700° C. The first scavenger cathode material, reagent grade lead (7 lb), was then placed in the cell and hydrogen treatment at red heat continued. The cell was transferred to a dry box containing a helium atmosphere in which all subsequent dismantling, filling, and assembling procedures were carried out. About 280 g lithium hydride was placed in the cell, which was evacuated, filled with hydrogen, and heated. It was found that too much decomposition occurred and use of lead as cathode was abandoned, to be replaced by an aluminum-lithium mixture (15 mole % Li). The hydrogen treatment was repeated, some hydrogen being absorbed and the cell charged with 1 lb of lithium hydride (Maywood Chem. Co. 10-20 mesh). The cell was heated to 700° C, as measured by the thermocouple in the alloy. After this treatment, the cell was once again dismantled and all lithium hydride removed. A fresh 1-lb charge of hydride was placed in the cell (for later experiments the cell was almost filled with hydride to cut down dead space). When thermal decomposition had settled down to a low rate at 670-675° C, electrolysis was started using a stabilized current of 1 amp. This was obtained from storage batteries supplying 110 v d-c. by means of dropping resistors and a ballast tube. Cell voltage was not controlled but was measured. Cell temperatures were controlled manually and stability was enhanced by use of a constant voltage transformer.

Electrolyses were run for periods up to 27 minutes, during which time gas volumes of the order of 100 cc at the measured constant cell pressure (580-740 mm Hg) were collected

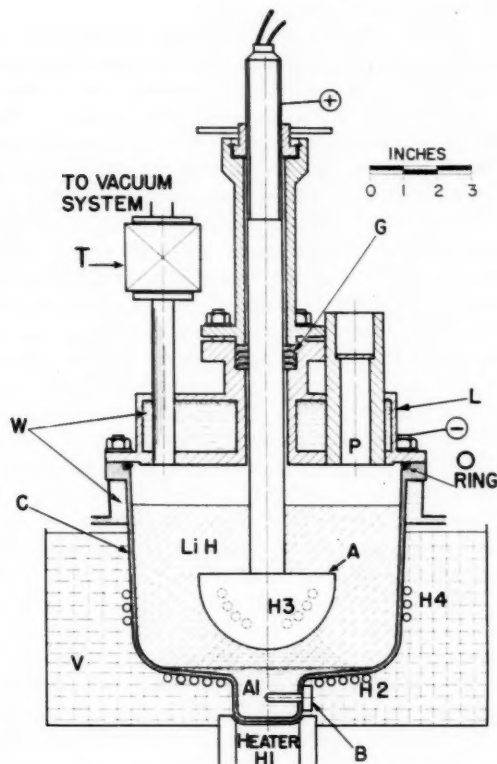


FIG. 1. Electrolysis cell.

C—Cell
L—Lid
A—Hemispherical anode
H₁₋₄—Heating elements
W—Water-cooling jackets

T—O-Ring high-vacuum valve (6).
P—Viewing port
V—Vermiculite
G—Teflon gaskets
B—Thermocouple well

in a burette. The rate of thermal decomposition or absorption was determined before and after each electrolysis and used to calculate the corrected amount of hydrogen evolved during electrolysis.

RESULTS AND DISCUSSION

With Lead as Scavenger:

Decomposition of lithium hydride shown by hydrogen evolution set in at about 350° C. Hydrogen had to be removed to keep the pressure in the system below atmospheric pressure. During subsequent cooling and reheating the onset of decomposition occurred at higher temperatures (500–550° C). The rate of gas evolution decreased somewhat as decomposition proceeded but was still high after 70% of the lithium hydride initially present had been decomposed. This system therefore does not attain hydrogen dissociation pressures below 1 atm at reasonable concentrations of lithium in the scavenger.

With Lithium-Aluminum as Scavenger:

Decomposition of lithium hydride occurred here too but after 1.2 moles had been decomposed the dissociation pressure settled down to somewhat less than an atmosphere at the operating temperatures. As the lithium content of the aluminum increased, higher temperatures were required for a given dissociation pressure. Working temperatures were chosen to give as low a rate of change of hydrogen evolution as possible, while maintaining a hydrogen pressure of 580–740 mm Hg. The other factor governing the choice of temperature was the electrical resistance of the electrolyte which with a cathode-anode separation of 1.5 cm was to be kept below 10 ohms. There was a rapid increase in resistance at temperatures below those shown in Table I. The rather large cell voltage fluctuations shown in the table for some of the runs were probably due to lack of homogeneity or local temperature instabilities in the melt. As mentioned previously the temperature measured was that of the alloy pool. In none of the experiments did the meter indications fluctuate wildly as found by Moers in the original electrolysis experiments.

From the results in Table I it appears to be rather difficult to prescribe optimum operating conditions for the electrolysis. The variables investigated were temperature, electrolysis time, and cell current. Temperature within the range studied, 670–689° C, does not seem to have too much effect. The other two variables are to some extent inter-related, since the electrolyses were run until a fixed amount of gas had been collected (100 or 127.5 cc at operating pressure), this gas, however, containing varying amounts of hydrogen produced by thermal decomposition. At first sight, the current efficiency seems to decrease with increasing duration of electrolysis, which would be in accord with the observations of Peters, and Potter and Bockris. Apparently electrolysis times of under 10 minutes correspond to yields of 60% and higher (Runs A1 to B9, E15 through F36) while electrolyses lasting for more than 20 minutes give yields of 40–50% (Runs E11 to D14). However, although the rate of electrolytic gas evolution was not usually measured, in two experiments (E16 and E17) where such measurements were made, the rate of volume increase was essentially constant for the whole period of the electrolysis. Hence the tentative supposition about a yield-time relation is not borne out in detail.

To the extent that the cell current is related to the electrolysis time, higher currents apparently correspond to better yields. This generalization does not fit experiments A1 to A8. The possibility that the higher yields in runs using 2 amp (E15 to F36) were artifacts due to thermal decomposition of the hydride by the heat liberated by the current is discounted (i) by experiments A7 and 8 where good yields were obtained with 0.29 amp, and (ii) by experiments B12 to B15 where the wattage dissipated was higher than in the 2-amp runs and much poorer yields resulted.

A possible explanation of the results discussed in the preceding paragraphs may be that the scavenger cathode is only partially effective: effective enough to make it possible to electrolyze lithium hydride near its melting point profitably for much longer periods than those used by Potter and Bockris but not quite able to prevent some lithium from getting into the melt. This would account for the apparent irregular yields and also for some of the cell voltage variations.

Hydrogen-Deuterium Separation:

Exchange of hydrogen with lithium hydride takes place slowly at room temperature (7) by means of a surface reaction and a diffusion process and would be expected to proceed much more rapidly at the working temperatures used here, where the additional mechanisms of dissociation and recombination are available. It was, however, of theoretical and practical interest to see whether one could detect any electrolytic separation

TABLE I
ELECTROLYSIS DATA

| Electrolysis No. | Temperature, °C | Electrolysis time, minutes | Cell current, amp | Cell voltage, volts | Vol. of electrolytic gas at n.t.p., cc | Average thermal decomposition (absorption) rate cc/minute at n.t.p. | Current yield, % |
|------------------|-----------------|----------------------------|-------------------|---------------------|----------------------------------------|---------------------------------------------------------------------|------------------|
| A1 | 672.0→671.5 | 6.4 | 1.08 | 3.0→2.8* | 27 | 7.0 | 56 |
| A2 | 671.5 | 6.2 | 1.08 | 3.2 | 43 | 5.7 | 82 |
| A3 | 672.0 | 10.6 | 0.99 | 4.2→4.6 | 75 | 0.2 | 103 |
| A4 | 671.5→671.6 | 9.9 | 0.98 | 5.0→5.5 | 78 | 0.0 | 115 |
| A5 | 671.6→671.7 | 10.0 | 0.98 | 5.9→6.2 | 79 | 0.0 | 115 |
| A6 | 671.7 | 10.5 | 0.98 | 6.6→7.1 | 80 | 0.0 | 111 |
| A7 | 671.7 | 10.0 | 0.29 | 2.6→2.7 | 23 | 0.1 | 114 |
| A8 | 671.5→672.2 | 8.0 | 0.29 | 2.8→2.9 | 17 | 0.9 | 107 |
| B9 | 672.8 | 8.1 | 1.00 | 8.4→9.5 | 50 | 3.7 | 89 |
| B10 | 670.4 | 17.2 | 1.00 | | 69 | 1.1 | 57 |
| B11 | 670.6 | 20.4 | 1.00 | | 62 | 1.2 | 44 |
| B12 | 670.7 | 20.5 | 0.99-1.00 | 15→12.3 | 63 | 1.2 | 45 |
| B13 | 671.0→671.5 | 21.8 | 0.98 | 14.7±2 fluc. | 60 | 1.3 | 40 |
| B14 | 671.0→670.3 | 26.8 | 0.98 | 14.0±1.6 | 61 | 1.0 | 33 |
| B15 | 670.0→671.7 | 26.4 | 0.96 | 16.0±1.0 | 71 | 0.6 | 40 |
| C1 | 677.1→677.4 | 21.0 | 1.05 | 4.3→5.4 | 63 | 2.2 | 41 |
| C2 | 677.4 | 20.8 | 1.05 | 5.4 | 70 | 1.9 | 46 |
| C3 | 677.6 | 20.8 | 1.05 | 5.6→5.4 | 82 | 1.3 | 54 |
| C4 | 677.9 | 21.8 | 1.05 | 5.4→5.2 | 85 | 1.1 | 53 |
| C5 | 677.9 | 20.4 | 1.05 | 5.1→5.0 | 86 | 1.1 | 58 |
| C6 | 678.1 | 22.4 | 1.05-1.06 | 5.0→4.8 | 81 | 1.2 | 49 |
| C7 | 678.3 | 22.0 | 1.06 | 4.8 | 89 | 0.9 | 55 |
| D8 | 678.8 | 21.2 | 1.08-1.09 | 6.3±0.1 | 78 | 1.6 | 49 |
| D9 | 678.9 | 22.5 | 1.08 | 6.5→5.2 fluc. | 84 | 1.3 | 49 |
| D10 | 679.2 | 23.1 | 1.08 | 5.6→5.2 | 84 | 1.2 | 48 |
| D11 | 679.8 | 23.5 | 1.08 | 5.4→5.1 | 86 | 1.1 | 49 |
| D12 | 680.0 | 25.6 | 1.08 | 5.0→4.8 | 89 | 0.9 | 46 |
| D13 | 680.2 | 26.0 | 1.08 | 5.0→4.8 | 101 | 0.4 | 52 |
| D14 | 680.2 | 27.0 | 1.08 | 5.0→4.8 fluc. | 110 | 0.1 | 54 |
| E15 | 684.9 | 10.0 | 2.05 | 6.8→6.5 | 94 | 0.7 | 66 |
| E16 | 685.1 | 9.4 | 2.05-2.08 | 6.2→5.6 | 99 | 0.2 | 73 |
| E17 | 686.0 | 9.4 | 2.07-2.09 | 5.6→5.0 | 100 | 0.0 | 74 |
| E18 | 686.7 | 9.5 | 2.07-2.08 | 5.2→4.5 | 104 | (0.4) | 76 |
| E19 | 687.6 | 9.7 | 2.08 | 4.9→4.2 | 106 | (0.6) | 76 |
| E20 | 688.3 | 10.9 | 2.08-2.09 | 4.4→3.8 | 111 | (1.0) | 70 |
| E21 | 688.5 | 9.2 | 2.09 | 4.0→3.6 | 108 | (1.0) | 81 |
| E22 | 688.5 | 9.4 | 2.09 | 3.8→3.5 | 92 | (0.2) | 67 |
| E23 | 688.5 | 10.8 | 2.09 | 3.8-3.6 | 89 | 0.1 | 57 |
| F24 | 686.8 | 6.7 | 2.01 | 4.5→4.2 | 70 | 1.1 | 74 |
| F25 | 686.2→685.8 | 7.1 | 2.01 | 4.6→4.4 | 69 | 1.0 | 70 |
| F26 | 685.4 | 7.5 | 2.01 | 4.8→4.6 | 73 | 0.4 | 70 |
| F27 | 685.4 | 7.7 | 2.01 | 4.9→4.6 | 77 | 0.0 | 72 |
| F28 | 685.1 | 8.2 | 2.01 | 5.1→4.7 | 82 | (0.6) | 71 |
| F29 | 685.1 | 9.3 | 2.01 | 4.8±0.4 fluc. | 85 | (0.9) | 65 |
| F30 | 685.1→684.9 | 9.1 | 2.01 | 5.2±0.4 fluc. | 83 | (0.8) | 66 |
| F31 | 684.9 | 9.1 | 2.01 | 5.5±0.5 fluc. | 83 | (0.8) | 65 |
| F32 | 684.9 | 9.7 | 2.01 | 6.0→5.5 | 83 | (0.8) | 61 |
| F33 | 685.1 | 10.3 | 2.01 | 6.4→5.5±0.2 fluc. | 83 | (0.7) | 57 |
| F34 | 685.1 | 10.2 | 2.01 | 6.8→6.0 | 85 | (1.0) | 60 |
| F35 | 685.2 | 8.7 | 2.00 | 7.2→6.2 | 87 | (1.5) | 72 |
| F36 | 685.4 | 9.3 | 2.00 | 7.4→6.2 | 81 | (0.8) | 63 |

Electrolyses A1-B15 were carried out with different LiH filling from C1-F36. Runs between which the cell had been cooled to room temperature and sometimes evacuated are designated by different letters.

*Arrow indicates drift during an experiment.

of the hydrogen isotopes. Mass spectrometric analyses of the hydrogen produced electrolytically (i.e. 59, 65, 76, 98, and 96% of the total gas collected in electrolysis series B, C, D, E, and F respectively) did not give significantly different deuterium-hydrogen ratios from those of the hydrogen produced by thermal decomposition. Thus if any separation occurred during the electrolysis it must have been masked by exchange.

The mass spectrometer analyses also showed that the gas contained only species of mass 2 and 3 and no significant amounts of species attributable to methane (from carbon in the steel), nitrogen, etc.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Mrs. K. O. Kutschke, National Research Council, Ottawa, and Mr. D. C. Austen, Atomic Energy of Canada Limited, Chalk River, for mass spectrometric analyses. They would also like to thank Dr. H. Sheffer, Dr. R. M. Heggie, and Dr. E. J. Casey for discussions.

REFERENCES

1. MOERS, K. *Z. anorg. u. allgem. Chem.* **113**, 179 (1920).
2. Peters, K. *Z. anorg. u. allgem. Chem.* **131**, 140 (1923).
3. POTTER, E. C. and BOCKRIS, J. O'M. *Colloq. intern. centre natl. recherche sci. (Paris)* **39**, Electrolyse C3-C6, (1952); *Chem. Abstr.* **47**, 5280c (1953).
4. ROGERS, R. R. and VIENS, G. E. *Trans. Can. Inst. Mining Met.* **51**, 273 (1948).
5. GIBB, T. R. P., Jr. and MESSER, C. E. A survey report on lithium hydride. U.S. Atomic Energy Comm. NYO-3957 (1954).
6. STARK, J. A. and LANGSDORF, A., Jr. *Rev. Sci. Instr.* **25**, 188 (1954).
7. WILZBACH, K. E. and KAPLAN, L. *J. Am. Chem. Soc.* **72**, 5795 (1950).

DONOR ACCEPTOR REACTIONS OF TITANIUM TETRACHLORIDE WITH FORMAMIDE AND N,N-DIMETHYL FORMAMIDE¹

JACQUES ARCHAMBAULT² AND ROLAND RIVEST

ABSTRACT

Co-ordination complexes of titanium tetrachloride with formamide and N,N-dimethyl formamide have been prepared. All the complexes found are explained through a co-ordination number of 6 for titanium (IV).

The infrared spectra of these compounds were measured; a negative shift observed for the carbonyl frequency and a positive shift observed for what is thought to be the C—N frequency are explained by a co-ordination through the oxygen of these molecules. Structural formulas are proposed for the compounds obtained.

INTRODUCTION

Titanium tetrachloride "A" is a very strong Lewis acid. Its reactions with donor molecules were very well summarized by Jackson (1) in 1939 and more recently by Archambault (2) in 1956. The only addition compound between "A" and an amide was prepared by Dermer and Fernelius (3). They reported the synthesis of an addition compound between "A" and N,N-diphenylacetamide, but the elementary analysis is the only evidence they have to support the proposed formula $\text{TiCl}_4 \cdot 2\text{CH}_3\text{CON}(\text{C}_6\text{H}_5)_2$.

An amide, even with two donor atoms, oxygen and nitrogen, should not give a chelate with "A" because it would be a four-atom ring which is very seldom obtained (4). The bonding through both donors could lead to a polymeric species, but the molecular weight determination of one complex obtained indicated that this is not the case. So the remaining question to answer is the following: which atom in the donor molecule is complexed with "A"? Infrared spectra of some metal-urea complexes have been measured by Mizushima and Quagliano (5). They reveal that urea forms nitrogen-to-metal bonds with some transition metals and oxygen-to-metal bonds with others. Since the relative ability of the two donors is easily reversed by passing from one complex to another, it seemed to us that experimentation was the best way to get an answer to our question. N,N-dimethyl formamide was chosen for this purpose.

Furthermore, it is well known that substitution reactions occur very easily when the donor atom, oxygen or nitrogen, is combined with a more or less labile hydrogen. We had hoped that the use of formamide as a donor would give us additional information and lead to the answer of the previous question. It was also of interest to know if the strong molecular association of formamide would have any effect on the reaction.

EXPERIMENTAL

Materials and Manipulations

Reagent grade titanium tetrachloride was purified by the method of Gilchrist (6), redistilled, and used as such. The reagent grade of the amides and of the solvents used for infrared measurements was carefully dried over sodium sulphate and redistilled under completely dry atmosphere; the medium fraction was used for our experiments.

Titanium tetrachloride and its addition compounds are extremely sensitive to moisture, so all the experiments were performed under controlled atmosphere using dry nitrogen. Unless otherwise indicated, the addition of the titanium tetrachloride was made through

¹Manuscript received June 10, 1958.

²Contribution from the Department of Chemistry, University of Montreal, Montreal, Que.

³Fellow of l'Office Provincial des Recherches Scientifiques de la Province de Québec.

a pressure-equalizing funnel and the reaction was allowed to take place in a closed system previously flushed with nitrogen. Agitation was provided with a Teflon-enclosed magnetic stirrer.

The System: $\text{TiCl}_4\text{-HCON}(\text{CH}_3)_2$

A solution of TiCl_4 in carbon tetrachloride was added dropwise to excess dimethyl formamide diluted in the same solvent. The reaction product, washed with carbon tetrachloride and dried under vacuum, is a yellow powder, much more stable to moisture than most adducts of TiCl_4 with organic molecules. The high melting point of this complex ($220\text{--}225^\circ\text{C}$) is another evidence of its greater stability. The compound is soluble in polar solvents with or without decomposition, according to the donor ability of the solvent molecule. The analyses for titanium and chlorine were made gravimetrically on the same sample, the titanium being weighted as TiO_2 and the chlorine as AgCl . Carbon and hydrogen were determined by the conventional microcombustion technique and nitrogen by the Kjeldal method.

| | % Ti | % Cl | % N | % C | % H | Ti/Cl |
|------------------------------------------------------------|-------|-------|------|-------|------|--------|
| Calc. for $\text{TiCl}_4\cdot 2\text{HCON}(\text{CH}_3)_2$ | 14.26 | 42.22 | 8.34 | 21.42 | 4.20 | 1/4.00 |
| Found | 14.20 | 41.78 | 8.27 | 21.44 | 4.50 | 1/3.97 |

Ebullioscopic measurements were carried out on methylene chloride solutions of the adduct, using a Swietowslawski boiling-point apparatus. The molecular weight so found (340 ± 15) is in good agreement with the formula weight (335.9) of the monomeric species. Then the idea of a polymeric chain through both donor atoms is to be rejected. Moreover, if we are to maintain the generally admitted co-ordination number of 6 for titanium (IV), we must exclude the possibility that both nitrogen and oxygen act as donors towards the same titanium atom. This will be confirmed by infrared spectrum investigations.

The System: $\text{TiCl}_4\text{-HCONH}_2$

A saturated solution of formamide in methylene chloride was added dropwise to a solution of TiCl_4 in the same solvent, so that the reaction medium was always in excess of "A". The reaction product is a yellow powder insoluble in methylene chloride from which it was separated by filtration. After being washed many times with fresh anhydrous CH_2Cl_2 , it was dried under vacuum at room temperature. This product is much less stable to moisture than its dimethyl formamide congener. It has no definite melting point, but decomposes on heating with loss of HCl . An attempt to determine nitrogen by the micro Dumas method was unsatisfactory, but the Kjeldal method gave reliable results.

| | % Ti | % Cl | % N | % C | % H | Ti/Cl |
|------------------------------------------------|-------|-------|-------|------|------|--------|
| Calc. for $\text{TiCl}_4\cdot 2\text{HCONH}_2$ | 17.12 | 50.69 | 10.01 | 8.58 | 2.16 | 1/4.00 |
| Found | 17.42 | 49.43 | 9.88 | 9.44 | 2.39 | 1/3.78 |

The product is soluble only in highly polar solvents in which the possibility of decomposition due to interchange with the solvent molecules is not to be disregarded. Another restriction which should not be neglected is that ebullioscopic measurements on this adduct require a low-boiling solvent in order to avoid decomposition by heat. So molecular weight determinations could not be made because of the absence of a suitable solvent either for ebullioscopic or cryoscopic experiments.

Attempts to perform the reaction between pure reactants resulted in somewhat different compounds. In a first experiment, excess TiCl_4 has been slowly added to pure formamide at the temperature of 0°C . The reaction, which is highly exothermic, rapidly yields a yellow spongy solid. After being thoroughly washed with CCl_4 to remove excess TiCl_4 , and dried under vacuum, this substance yielded a hygroscopic yellow product, the composition of which changed with varying drying temperature. We have found it pretty hard to repeat our results from one experiment to the other as shown in Table I. However, at room temperature, it appears that no substitution occurs, and one finds a compound of the following formula $\text{TiCl}_4 \cdot (\text{HCONH}_2)_2 \cdot n\text{HCONH}_2$ in which " n " varies from 3.5 to 4.5. This does not imply an exception to the normal co-ordination number of 6 for titanium (IV), but simply that we are dealing with the same hexa-co-ordinated compound more or less associated through hydrogen bridging, according to the following scheme.

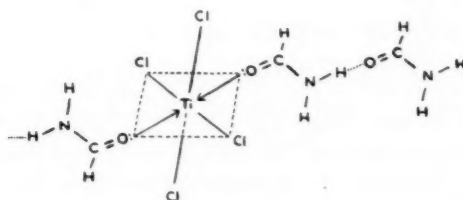


FIG. 1.

TABLE I

| Drying temp. | | % Ti theor. | % Ti found | % Cl theor. | % Cl found | Ti/Cl theor. | Ti/Cl found |
|--------------|------------------------------------------------------------|-------------|----------------|-------------|----------------|--------------|------------------|
| 20° C | $\text{TiCl}_4 \cdot 4\text{HCONH}_2$ | 12.90 | 11.53 12.84 | 38.40 | 35.44 38.20 | 1/4 | 1/4.1 1/3.99 |
| 50° C | $\text{TiCl}_4 \cdot 3\text{HCONH}_2$ | 14.75 | 14.24 14.28 | 43.73 | 40.01 40.69 | 1/4 | 1/3.79 1/3.84 |
| 100° C | $\text{TiCl}_4 \cdot \text{HCONH}_2 \cdot 2\text{HCONH}_2$ | 16.28 | 16.22 | 38.90 | 37.81 | 1/3 | 1/3.15 |

If the drying temperature is increased, the composition changes gradually till one gets a ratio of Cl/Ti of 3.15 with approximately one mole of HCl and one mole of formamide pumped off.

Infrared Spectra and Structure Discussions

The infrared spectra were obtained by a Perkin-Elmer model 112 single beam spectrophotometer using NaCl prism. Characteristic absorption bands of $\text{TiCl}_4 \cdot 2\text{HCON}(\text{CH}_3)_2$ are given in Table II, together with those of N,N-dimethyl formamide in different solvents.

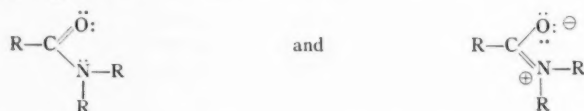
From the spectra of $\text{TiCl}_4 \cdot 2\text{HCON}(\text{CH}_3)_2$ and $\text{HCON}(\text{CH}_3)_2$ in methylene chloride and acetonitrile, the $\text{C}=\text{O}$ stretching frequency of the complex is shown to be shifted by about 30 cm^{-1} to lower frequencies. A similar shift of the carbonyl band in complex compounds is an indication of co-ordination through the oxygen atom (5). Corresponding data for the adduct with formamide are recorded in Table III.

Once again, the carbonyl band is shifted by the amount of 28 cm^{-1} to lower frequencies. This is certainly a strong indication that co-ordination of either substituted or unsubstituted amides to titanium (IV) is made through oxygen rather than nitrogen.

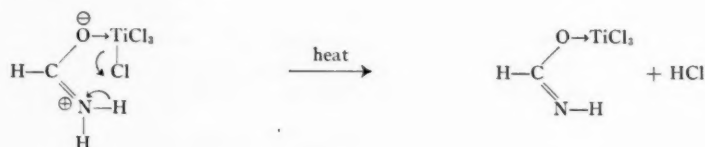
TABLE II
 ABSORPTION MAXIMA IN cm^{-1} OF $\text{TiCl}_4 \cdot 2\text{HCON}(\text{CH}_3)_2$ AND $\text{HCON}(\text{CH}_3)_2$

| Band assignment | in CH_2Cl_2 | | | in CH_3CN | | |
|-----------------------------------|---------------------------------------------------|------------------------------|------------------|---------------------------------------------------|------------------------------|------------------|
| | $\text{TiCl}_4 \cdot 2\text{HCON}(\text{CH}_3)_2$ | $\text{HCON}(\text{CH}_3)_2$ | Fre-quency shift | $\text{TiCl}_4 \cdot 2\text{HCON}(\text{CH}_3)_2$ | $\text{HCON}(\text{CH}_3)_2$ | Fre-quency shift |
| C=O stretching vibration | 1646 vs | 1676 vs | -30 | 1648 vs | 1676 vs | -28 |
| | 1372 ± 5 m | 1386 ± 5 m | | — | — | — |
| | — | — | — | 1249 m | 1258 m | - 9 |
| Possible C—N stretching vibration | 1123 m | 1093 m | +30 | 1123 m | 1095 m | +28 |
| | 1062 w | 1064 w | -2 | — | — | — |

Nevertheless, since the contribution of the tautomeric form $\text{H}-\text{C} \begin{smallmatrix} \text{OH} \\ \text{NH} \end{smallmatrix}$ to formamide is negligible (7, 8) one could argue that the loss of HCl observed on heating the formamide adduct is an evidence of co-ordination by nitrogen. Indeed, this internal rearrangement generally implies that the donor atom is bonded to a more or less labile hydrogen, but in the case of formamide, it can be accounted for otherwise in terms of the resonance theory. As pointed out by Pauling (9) and Dewar (10), amides are in resonance between the two following forms:



The dipolar form contributes about 15% (8). The formation of a co-ordinated link through the free electron pair of nitrogen would result in the loss of the resonance energy of the parent base which amounts to 21 kcal/mole in formamide (9). However, the formation of $\text{O} \rightarrow \text{Ti}$ bonds is expected to increase the contribution of the dipolar structure (11, 12), so the positive formal charge on nitrogen eases the departure of a proton, according to the following mechanism:



On the other hand, if the effect of a Lewis acid on amides is to result in a greater double-bond character for the nitrogen-to-carbon bond and a greater single-bond character for the carbon-to-oxygen bond, one should be able to detect these effects by infrared spectra. As we have shown above, we observed a lowering of the $\text{C}=\text{O}$ stretching frequency in both adducts, but unfortunately, the position of the $\text{C}-\text{N}$ stretching band is not as well

known. In fact, no data are available concerning the assignment of infrared absorption bands of N,N-dimethyl formamide.

Infrared spectrum of formamide has been more thoroughly investigated, and the position of the C—N stretching band is assumed to be at 1309 cm^{-1} in the liquid state, which is supported by the positive frequency shifts of this band accompanying the passage from vapor to liquid state and from formamide to formamide hydrochloride (13).

As shown in Table II, there is only one band of N,N-dimethyl formamide which suffers a positive shift when co-ordinating to titanium (IV), and this shift is of the same order, but opposite in direction, as the shift due to the lowering of the carbonyl frequency. This band is located at 1086 cm^{-1} in a non polar solvent like CS_2 and shifted to 1093 and 1095 cm^{-1} in CH_2Cl_2 and CH_3CN . Furthermore, its frequency increases by some $28\text{--}30\text{ cm}^{-1}$ when entering complexes. Such a behavior appears to be an argument in favor of its assignment to the C—N stretching vibration, although this tentative assignment needs to be checked by model compounds.

Moreover, the lack of a suitable solvent for the adduct $\text{TiCl}_4 \cdot 2\text{HCONH}_2$ prevented us from finding out the exact position of its C—N band, which is well known for pure formamide. Emulsions were not too good in Nujol, and light diffusion occurred. Nevertheless, the C—N band appeared to be much broader and centered over higher frequencies, although it is difficult to estimate the value of the shift.

CONCLUSIONS

The results of elementary analysis, molecular weight determinations, and infrared measurements have led us to propose the following formulas for the compounds prepared:

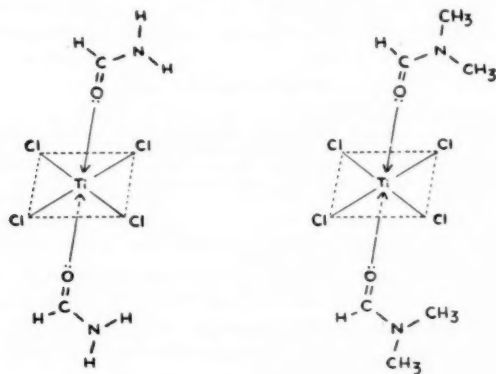


FIG. 2.

The corresponding *cis* forms are also a possibility.

ACKNOWLEDGMENTS

The authors are grateful to the following for their assistance: Prof. Camille Sandorfy for valuable discussions on the infrared spectra measured, the National Research Council of Ottawa for its financial assistance (R.R.), and l'Office Provincial des Recherches Scientifiques de la Province de Québec for a fellowship to one of us (J.A.).

TABLE III
 ABSORPTION MAXIMA IN cm^{-1} OF $\text{TiCl}_4 \cdot 2\text{HCONH}_2$ AND HCONH_2

| Band assignment | Emulsions in Nujol | | Solutions in CH_3CN | | Frequency shift |
|------------------------------------------|---------------------------------------|------------------|---------------------------------------|------------------|-----------------|
| | $\text{TiCl}_4 \cdot 2\text{HCONH}_2$ | HCONH_2 | $\text{TiCl}_4 \cdot 2\text{HCONH}_2$ | HCONH_2 | |
| NH_2 sym. and asym. vibrations | 3375–3100 m | 3400–3200 s | — | 3467 m | |
| | | | | 3360 m | |
| $\text{C}=\text{O}$ stretching vibration | — | 1683 vs | 1676 vs | 1704 vs | –28 |
| | 1550 \pm 10 s | 1645–1580 m | | | |
| | — | 1392 s | | | |
| $\text{C}-\text{N}$ stretching vibration | 1370–1300 | 1312 s | — | 1282 s | |
| | 1090 m | — | | | |
| | 1052 w | 1052 w | | | |

RÉSUMÉ

On a préparé des complexes de coordination du tétrachlorure de titane avec la formamide et la N,N-diméthyl formamide. Tous les complexes isolés sont expliqués en attribuant au titane (IV) le nombre de coordination 6. Les spectres infrarouges de ces composés ont été mesurés. Une variation négative de la fréquence du carbonyle et une variation positive d'une bande attribuée à la vibration C—N sont expliquées en supposant que la coordination au titane se fait par l'oxygène des molécules d'amide. On propose des formules dans l'espace pour les composés préparés.

REFERENCES

1. JACKSON, K. E. *Chem. Revs.* **25**, 67 (1939).
2. ARCHAMBAULT, J. Thèse de Maîtrise, Université de Montréal, Montréal, Québec. 1956.
3. DERMER, O. C. and FERNELIUS, W. C. *Z. anorg. u. allgem. Chem.* **221**, 83 (1934).
4. MOELLER, T. *Inorganic chemistry*. John Wiley & Sons, Inc., New York. 1952. p. 236.
5. PENLAND, R. B., MIZUSHIMA, S., CURRAN, C., and QUAGLIANO, J. V. *J. Am. Chem. Soc.* **79**, 1575 (1957).
6. CLABAUGH, W. S., LESLIE, R. T., and GILCHRIST, R. J. *Research Natl. Bur. Standards*, **55**, 261 (1955).
7. WHELAND, G. W. *Resonance in organic chemistry*. John Wiley & Sons, Inc., New York. 1955. p. 410.
8. LENORMANT, H. *Bull. soc. chim. France*, 33 (1948).
9. PAULING, L. *Nature of the chemical bond*. Cornell Univ. Press, Ithaca, N.Y. 1945. p. 207.
10. DEWAR, M. J. S. *The electronic theory of organic chemistry*. The Clarendon Press, Oxford. 1949. p. 96.
11. YAMAGUCHI, A. *et al.* *J. Am. Chem. Soc.* **80**, 527 (1958).
12. DAVIES, M., EVANS, J. C., and JONES, R. L. *Trans. Faraday Soc.* **51**, 761 (1955).
13. EVANS, J. C. *J. Chem. Phys.* **22**, 1228 (1954).

THE HEMICELLULOSE OF WHITE ELM (*ULMUS AMERICANA*) II. CONSTITUTION OF THE METHYL GLUCURONO-XYLAN¹

J. K. GILLHAM AND T. E. TIMELL

ABSTRACT

The wood of white elm (*Ulmus americana*) has been found to contain less xylan than most other hardwoods. Partial hydrolysis of the hemicellulose component yielded an aldatriuronic acid, a glucuronosyl xylose, 2-*O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-D-xylopyranose, 4-*O*-methyl-D-glucuronic acid, and galacturonic acid.

Hydrolysis of the fully methylated polysaccharide gave a mixture of 2-*O*- and 3-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, 2,3,4-tri-*O*-methyl-D-xylose, and 2-*O*-(2,3,4-tri-*O*-methyl- α -D-glucopyranosyluronic acid)-3-*O*-methyl-D-xylopyranose in a molar ratio of 6:124:1:14. The number-average degree of polymerization of the methylated hemicellulose was 133 and that of the native polymer 185. On the basis of this and other evidence it is suggested that the xylan is linear and contains 185 1,4-linked β -D-xylopyranose residues, every seventh of which carries a single terminal side chain of 4-*O*-methyl-D-glucuronic acid attached by an α -glycosidic bond through C₂ of the xylose. The number of acid groups is larger than in other hardwood hemicelluloses so far studied.

In a previous investigation (1) it was shown that partial hydrolysis of a hemicellulose from white elm yielded a mixture of sugars containing xylose, 2-*O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-D-xylopyranose, and several other uronic acids. The present paper is concerned with the nature of these sugar acids and with the structure and properties of the hemicellulose.

RESULTS AND DISCUSSION

Resolution of the mixture of sugar acids referred to previously (1) on a column of anion exchange resin yielded six fractions. The first acid to be eluted from the column (I) contained one methoxyl and one carboxyl group. Examination by paper chromatography after partial hydrolysis suggested the presence of xylose, a mono-*O*-methyl glucuronic acid, and the above aldobiouronic acid. Together with the equivalent weight (510) these facts indicated that I ($[\alpha]_D^{20} + 75^\circ$) was a triouronic acid containing two xylose and one mono-*O*-methyl glucuronic acid residue. A similar triouronic acid has been isolated from trembling aspen (2), western hemlock (3), Monterey pine (4), loblolly pine (5), and milkweed floss (6).

The second acid obtained (II) was the aldobiouronic acid referred to above. The following fraction was further resolved by paper chromatography and elution from a coconut charcoal column (7). The first of the three acids thus obtained (III) was characterized as galacturonic acid after reduction to galactose. Acid IV contained no methoxyl group. Chromatographic examination indicated the presence in the hydrolyzate of glucuronic acid, glucuronolactone, and xylose. These results, together with the equivalent weight (354), suggested the presence of an aldobiouronic acid ($[\alpha]_D^{20} + 85^\circ$) containing one glucuronic acid and one xylose residue. Such acids have frequently been isolated after partial hydrolysis of many non-woody plants, for example wheat straw (8). In wood, glucurone alone has so far been encountered in hydrolyzates from trembling aspen (9), black spruce (10), and white birch (11).

The next acid (V) was not further examined but the last (VI), which contained one methoxyl and one carboxyl group, was converted to the methyl ester, methyl glycoside,

¹Manuscript received July 14, 1958.

Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.

reduced with lithium aluminum hydride and hydrolyzed to yield 4-*O*-methyl-D-glucose, identified through its crystalline osazone. Acid VI was therefore 4-*O*-methyl-D-glucuronic acid, a common constituent of plant hemicelluloses (12). Its infrared spectrum was identical with that of an authentic specimen.

The elm wood was analyzed by standard methods (12) and found to contain cellulose (49.3), lignin (23.6), acetyl (3.9), ash (0.3), uronic anhydride (3.6), galactan (0.9), mannan (2.4), araban (0.6), and xylan (11.5%). The content of xylan was exceptionally low for a hardwood and, for example, less than half of that of white birch (13).

The hemicellulose was isolated by direct alkaline extraction of the wood as described previously (1). Earlier evidence suggested strongly that the polysaccharide possessed residues of 4-*O*-methyl-D-glucuronic acid linked to xylose. If this were so, the uronic anhydride content corresponded to 7.0 xylose residues per acid group and the methoxyl content to 7.2. The corresponding value obtained from the equivalent weight of the acidic polysaccharide was 6.8.

The fully methylated hemicellulose was subjected to methanolysis under conditions which were known to effect no cleavage of the aldobiouronic acid. The glycosides were resolved into an acidic and a neutral fraction on a column of ion exchange resin. The acidic fraction, which contained only one component, was converted to the ester glycoside, reduced, and hydrolyzed to give a mixture of reducing sugars which was resolved on a charcoal column, yielding 2,3,4-tri-*O*-methyl-D-glucose and 3-*O*-methyl-D-xylose, both of which were characterized through their aniline derivatives. The acid was accordingly 2-*O*-(2,3,4-tri-*O*-methyl- α -D-glucopyranosyluronic acid)-3-*O*-methyl-D-xylopyranose. The fact that the 4-position was unsubstituted in this acid but was substituted when the free acid itself was methylated (1) showed that its xylose moiety was linked to other sugar residues through C₄. This, in conjunction with the absence of any 3,4-di-*O*-substituted xylose, suggested that the acid side groups were attached directly to the framework of the hemicellulose.

The solution of the neutral glycosides was extracted with chloroform for removal of any highly substituted and therefore volatile xyloside (14). After concentration of the extract and the remaining aqueous solution, the glycosides were again combined and hydrolyzed and the resulting mixture of reducing sugars was resolved by fractional extraction of its aqueous solution with chloroform. The first compound to be extracted was identified as 2,3,4-tri-*O*-methyl-D-xylose through its aniline derivative. The major component, which was only sparingly soluble in chloroform, crystallized and was identified as 2,3-di-*O*-methyl-D-xylose. A mixture of two mono-*O*-methyl xyloses was recovered from the aqueous phase and resolved by paper ionophoresis to yield 2-*O*- and 3-*O*-methyl-D-xylose. The molar ratio among the mono-*O*-methyl xyloses, the 2,3-di-*O*-methyl-D-xylose, and the 2,3,4-tri-*O*-methyl-D-xylose was determined as 6:124:1 (15). The yield of the acid fragment, 14 moles per non-reducing end group, corresponded to 10 xylose residues per acid group, a value higher than expected. The reason for this was probably a loss of uronide material during the methylation. Similar observations have been made elsewhere (16, 17, 18).

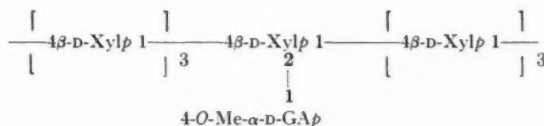
The large amount of 2,3-di-*O*-methyl-D-xylose isolated indicated that the backbone of the polysaccharide was composed of xylopyranose residues linked through positions 1 and 4, while the high negative rotation (-70°) of the hemicellulose suggested that the anhydroxylose units were present in the β -configuration. The 2,3,4-tri-*O*-methyl-D-xylose evidently originated from the non-reducing end groups. The side chains consisted of 1,2-linked 4-*O*-methyl-D-glucuronic acid residues, all of which were recovered as the

partly methylated aldobiouronic acid. The presence of the mono-*O*-methylated xyloses was therefore due to either incomplete methylation, demethylation, or branching.

When the number-average molecular weight of the methylated hemicellulose was determined by osmometry (19), a value of 24,000 was obtained. Assuming one 4-*O*-methyl-D-glucuronic acid group to be associated with 10 xylose residues, this corresponded to a degree of polymerization of 133. The number of non-reducing end groups indicated a number-average D.P. of 145, thus precluding the possibility of any branching. The presence of the mono-*O*-methyl xyloses was accordingly due to incomplete methylation or demethylation. Such phenomena have frequently been encountered elsewhere (16, 18, 20).

The hemicellulose was converted to the fully substituted acetate derivative without any apparent depolymerization (21). Osmotic pressure measurements indicated a number-average molecular weight of 45,900. Assuming the presence of seven anhydroxylose units for each acidic side group, this corresponded to a number-average degree of polymerization (\bar{P}_n) of 185. Intrinsic viscosities ($[\eta]$) were determined in cupriethylenediamine and in dimethyl sulphoxide. Application of a relationship developed for a similar hemicellulose (19) gave \bar{P}_n values of 236 and 193, respectively. These somewhat higher values were probably due to the approximate nature of the constant relating $[\eta]$ and \bar{P}_n .

Summarizing the above evidence, a simplified structure can now be suggested for the main hemicellulose component in white elm wood. This methyl glucurono-xylan evidently contains an average of 185 β -D-xylopyranose residues linked together by 1,4-glycosidic bonds to linear macromolecules. Every seventh, on the average, anhydroxylose unit carries a single, terminal side chain of 4-*O*-methyl-D-glucuronic acid, attached by an α -glycosidic linkage to C₂ of the xylose. In the native state most of the hydroxyl groups of the polysaccharide are probably esterified with acetic acid (22).



The constitution of the hemicellulose of white elm is similar, albeit not identical, to that of other methyl glucurono-xylans isolated from deciduous woods. These polysaccharides are all, with one possible exception (23), linear, and contain side chains of α -1,2-linked 4-*O*-methyl-D-glucuronic acid residues. Of the species so far studied, European (24) and American (23) beech, white birch (16), yellow birch (25), sugar maple (25), and trembling aspen (26) all contain hemicelluloses with 10–11 xylose residues per acid side group. The present hemicellulose apparently possesses relatively more acid side chains. In this respect it is, actually, more similar to the methyl araboglucurono-xylans present in coniferous woods, which contain more acid groups than the hardwood xylans. Western hemlock, for example, has been reported (27) to contain 4.3 xylose residues for each 4-*O*-methyl-D-glucuronic acid, European larch (28) 5–6, loblolly pine (29) 6–7, and Norway spruce (30) 5 and (31) 5.4, respectively. A methyl glucurono-xylan which also possesses 7 xylose residues per each 4-*O*-methyl-D-glucuronic acid is present in kapok (32), whereas another seed hair, namely milkweed floss (6), contains only half as many of the same acid groups.

It is interesting to note in this connection that white elm is more similar to softwoods than to hardwoods also in its low content of xylan (11.3%). Judging from the limited

number of species so far studied, it appears as if a relatively low content of xylan in a wood is usually associated with a larger number of acid side groups in the latter. Inspection of some recently published analytical data (13) indicates that the uronic anhydride content is rather constant for most woods in spite of the fact that the content of xylan varies considerably and is generally much lower for the conifers than for the woody angiosperms. A strict comparison is not possible, however, since a portion of the uronic anhydride is always derived from pectic material in the wood (33).

The number-average degree of polymerization of the present hemicellulose is only slightly lower than that of a similar polysaccharide from white birch, namely 197 (19), and is approximately the same as that of the methyl glucurono-xylans present in sugar maple (25) and yellow birch (25). Unfortunately, no reliable data are presently available as to the weight-average molecular weight of any native wood xylan.

EXPERIMENTAL

General experimental conditions, analytical procedures, and solvents used for separating sugars were the same as described previously (1, 12, 16). All specific rotations are equilibrium values and melting points are corrected. Evaporations were carried out *in vacuo* at temperatures not exceeding 50° C.

Preliminary Characterization of Acid I

This was the first acid to be eluted from the column of ion exchange resin referred to in the previous paper (1). Partial hydrolysis of the partly crystalline material, followed by examination by paper chromatography (solvent A), indicated the presence of xylose, 4-O-methyl-D-glucuronic acid, aldobiouronic acid, and unhydrolyzed triouronic acid. Anal. Calc. for $C_{17}H_{23}O_{15} \cdot 3H_2O$: OCH_3 , 5.9%; equiv. wt., 472. Found: OCH_3 , 4.8%; equiv. wt., 510; $[\alpha]_D^{20} +75^\circ$ (c, 1.0 in water).

Separation of Acids II-V

The eluate constituting the second main fraction from the ion exchange column was evaporated to dryness (250 mg) and resolved on three large sheets of Whatman No. 1 filter paper (solvent A). In this way acid II (110 mg) and acid V (3 mg) were separated from two other acids, which were combined and resolved (7) on a cocoanut charcoal (50-200 mesh, product of Fisher Scientific Company, Fair Lawn, N.J.) column (1.5 × 1.5 cm). Acid II (80 mg) was eluted with 5-7% and acid IV (20 mg) with 7-8% aqueous ethanol.

Chromatographic Identification of Acid III

The rate of movement on the paper chromatogram of this acid was the same as that of galacturonic acid. The methyl ester, methyl glycoside, formed by boiling with 4% methanolic hydrogen chloride under reflux for 6 hours, was reduced with lithium aluminum hydride (34, 35). After hydrolysis, paper chromatography (solvent B) suggested the presence of galactose.

Preliminary Characterization of Acid IV

Partial hydrolysis with 0.5 N sulphuric acid at 100° C for 20 hours, followed by paper chromatography (solvent A), indicated the presence of unchanged IV together with glucuronic acid, glucuronolactone, and xylose. Anal. Calc. for $C_{11}H_{18}O_{11}$: OCH_3 , nil; equiv. wt., 326. Found: OCH_3 , nil; equiv. wt., 354; $[\alpha]_D^{20} +85^\circ$ (c, 1.8 in water).

Identification of Acid VI

Acid V was not further investigated because of the paucity of material available. Acid

VI (400 mg) was converted to the ester glycoside and reduced in dry tetrahydrofuran (25 ml) with a solution of lithium aluminum hydride (1 g) in the same solvent (30 ml). The neutral glycoside was hydrolyzed to give a sirup, chromatographically (solvent B) identical with 4-*O*-methyl-D-glucuronic acid. Anal. Calc. for $C_7H_{14}O_6$: OCH_3 , 16.0%. Found: OCH_3 , 15.9%; $[\alpha]_D^{20} + 63^\circ$ (c , 2.8 in water). The phenylosazone derivative (35, 36) had m.p. and mixed m.p. 157° and an infrared spectrum identical with that of an authentic specimen.

Characterization of the Hemicellulose

The hemicellulose was isolated as described before (1). Anal. Pentosan, 78.5%; uronic anhydride, 15.2% (potassium salt); OCH_3 , 2.62% (free acid); $[\alpha]_D^{20} - 70^\circ$ (c , 1.1 in 2% potassium hydroxide).

Methylation of the Hemicellulose

The hemicellulose (18 g) was stirred with water (75 ml) and 40% (w/w) sodium hydroxide (150 ml) was added in an atmosphere of nitrogen, followed by dimethyl sulphate (135 ml) over a period of 20 hours at a temperature of $0^\circ C$. This treatment was repeated five times. The partly methylated material was recovered in the usual way and dissolved in tetrahydrofuran (37). Powdered sodium hydroxide (200 g) was added, followed by dropwise addition of dimethyl sulphate (200 ml) over a period of 10 hours. This treatment was repeated once. After neutralization with acetic acid, tetrahydrofuran was removed by distillation and the precipitated hemicellulose was dissolved in chloroform and reprecipitated into petroleum ether. Anal. OCH_3 , 36.1%.

The product was dissolved in chloroform (100 ml) and to the solution dry dimethyl formamide (100 ml), silver oxide (5 g), and methyl iodide (10 ml) were added. The mixture was shaken in the dark for 36 hours after which silver oxide (5 g) and methyl iodide (10 ml) were added and shaking was continued for another 12 hours (38). Salts were removed by filtration, chloroform was added, and the solution was extracted with water for 4 days. It was then dried over calcium sulphate, filtered through Celite, and evaporated to 100 ml. Precipitation into petroleum ether yielded white fibers (9 g). Anal. OCH_3 , 38.1%; $[\alpha]_D^{20} - 62^\circ$ (c , 0.82 in chloroform). The infrared spectrum indicated negligible absorption at the hydroxyl frequency of 3500 cm^{-1} .

Methanolysis of the Methylated Hemicellulose and Separation of the Acidic Component

The fully methylated polysaccharide (5.0 g) was boiled under reflux with 2% methanolic hydrogen chloride (100 ml) for 8 hours. Neutralization with silver carbonate, purification with hydrogen sulphide, and filtration through Celite yielded a sirup of glycosides (5.9 g). The ester groups were saponified with *N* sodium hydroxide at room temperature for 15 hours. Acidic sugars were adsorbed on a column of Dowex 1-X4 (acetate) exchange resin which was washed with water until free of neutral sugars. The acidic component was eluted with 2 *N* acetic acid and the solution was evaporated to a brown solid (1.08 g).

Preparation, Reduction, and Hydrolysis of the Ester Glycoside of the Partially Methylated Aldobiouronic Acid

The methyl glycoside of the partially methylated acid was reconverted to the methyl ester by boiling under reflux with 2% methanolic hydrogen chloride for 8 hours. It was then reduced with lithium aluminum hydride and subjected to methanolysis followed by hydrolysis with *N* hydrochloric acid. Removal of the acid and evaporation yielded a sirup which, when examined by paper chromatography (solvent C), appeared to contain equimolar amounts of a tri-*O*-methyl glucose and a mono-*O*-methyl xylose.

Separation and Identification of 2,3,4-Tri-O-methyl-D-glucose and 3-O-Methyl-D-xylose

The above sirup was added to the top of a cocoanut charcoal column (1.5×5 cm). Elution with 10% aqueous ethanol gave a compound (263 mg) which corresponded by paper chromatography (solvent C) and paper electrophoresis in a borate buffer solution (39, 40) to 3-O-methyl-D-xylose. Anal. Calc. for $C_6H_{12}O_5 \cdot OCH_3$, 18.9%. Found: OCH_3 , 17.9%. The 3-O-methyl-N-phenyl-D-xylosylamine, when recrystallized from ethyl acetate-petroleum ether, had m.p. 135–136° C; $[\alpha]_D^{20} +118^\circ$ (c, 1.2 in ethyl acetate).

Elution with 20% aqueous ethanol gave a compound (206 mg) which was chromatographically identical with 2,3,4-tri-O-methyl-D-glucose. Anal. Calc. for $C_6H_{12}O_5 \cdot OCH_3$, 41.9%. Found: OCH_3 , 41.0%; $[\alpha]_D^{20} +75^\circ$ (c, 2.2 in water). The 2,3,4-tri-O-methyl-N-phenyl-D-glucosylamine had m.p. and mixed m.p. 146° C. Its infrared spectrum was identical with that of an authentic sample.

Separation of the Neutral Components of the Methylated Hemicellulose

The mixture of neutral glycosides (3.9 g) was extracted with chloroform and the aqueous and the chloroform solutions were concentrated separately, after which they were recombined and hydrolyzed with N sulphuric acid. After neutralization with barium carbonate and deionization (Amberlite IR-120 and Dowex 1-X4) the aqueous solution was exhaustively extracted with chloroform in a liquid-liquid extractor for 3 days, after which the extract was removed. Continued extraction of the aqueous solution with chloroform for 3 weeks, followed by concentration of the extract, gave a chromatographically pure di-O-methyl xylose. The remaining aqueous phase contained only mono-O-methyl xyloses. The first extract was dissolved in water and extracted with chloroform for 3 hours. Repetition of this process several times finally yielded a chromatographically pure tri-O-methyl xylose.

Preliminary Characterization of the Mono-O-methyl Xyloses

This fraction had a methoxyl content (18.0%) corresponding to that of a mono-O-methyl xylose. Ionophoresis in a borate buffer solution indicated the presence of 2-O- and 3-O-methyl-D-xylose, with the latter compound constituting the major part of the mixture.

Identification of 2,3-Di-O-methyl-D-xylose

Crystals, m.p. 78° C, formed slowly in the colorless sirup. Anal. Calc. for $C_7H_{14}O_5 \cdot OCH_3$, 34.8%. Found: OCH_3 , 34.8%; $[\alpha]_D^{20} +23^\circ$ (c, 2.0 in water). The 2,3-di-O-methyl-N-phenyl-D-xylosylamine, when recrystallized from ethyl acetate, had m.p. and mixed m.p. 141° C. Its infrared spectrum corresponded to that of an authentic specimen.

Partial Identification of 2,3,4-Tri-O-methyl-D-xylose

The sirup (20 mg) could not be induced to crystallize; $[\alpha]_D^{20} +20^\circ$ (c, 1.3 in water). The aniline derivative, m.p. 98° C, had an infrared spectrum identical with that of an authentic sample.

Spectrophotometric Analysis of the Neutral Components of the Methylated Hemicellulose

A small portion of the mixture of methylated neutral sugars was applied to strips of filter paper which were irrigated with solvent C. The different sugars were located with guide strips, eluted with water, and adjusted to a convenient volume. Concentrations were determined by the o-aminodiphenyl method (15). The average value of three determinations was used. The relation between absorbance and concentrations of the three methyl sugars had been determined previously (16).

Determination of the Molecular Weight of the Methylated Hemicellulose

The osmometer used was a Zimm-Myerson (41) instrument as modified by Stabin and Immergut (42). Gel cellophane membranes, which had never been allowed to dry, were kindly supplied by American Viscose Corporation, Marcus Hook, Pa. The solvent was a 9:1 (v/v) mixture of chloroform-ethanol and the temperature was $30 \pm 0.01^\circ \text{C}$. The osmotic pressure was determined at four different concentrations by the static method and the values of the reduced osmotic pressure, h/w , as plotted against w , were extrapolated to zero concentration (Table I). The number-average molecular weight, \bar{M}_n , was calculated from the relationship $\bar{M}_n = 25,700/(h/w)_0$ and the corresponding degree of polymerization, \bar{P}_n , from the relationship $\bar{P}_n = \bar{M}_n \cdot n/M_R$, where n was the number of xylose residues present per acid side chain and M_R was the molecular weight of the repeating unit of the fully methylated polysaccharide.

TABLE I
OSMOMETRY DATA FOR THE METHYLATED
HEMICELLULOSE

| w^* | h^\dagger | h/w |
|-------|-------------|-------|
| 5.132 | 6.942 | 1.353 |
| 4.537 | 6.186 | 1.364 |
| 3.536 | 4.436 | 1.254 |
| 2.550 | 3.090 | 1.212 |
| 0 | — | 1.07 |

*Concentration in g/kg solution.

†Osmotic height in cm solvent.

Preparation of the Acetyl Derivative of the Hemicellulose

Hemicellulose (5 g) and freshly distilled formamide (200 ml) were stirred for 5 hours, after which anhydrous pyridine (250 ml) was added followed by dropwise addition of acetic anhydride over a period of 5 hours. After being stirred over night, the gelatinous reaction mixture was poured into ice water with vigorous stirring and recovered as described by Carson and Maclay (21). A second esterification was carried out in the same way although without addition of formamide. The acetyl content of the fully acetylated product was 37.8% (43).

Determination of the Molecular Weight of the Acetylated Hemicellulose

The molecular weight of the acetylated, native hemicellulose was determined as described above for the methylated polysaccharide. The results are given in Table II.

Viscosity Measurements

Relative viscosities were determined with a Craig-Henderson viscometer (44) and

TABLE II
OSMOMETRY DATA FOR THE ACETYLATED
HEMICELLULOSE

| w | h | h/w |
|-------|-------|-------|
| 3.238 | 2.053 | 0.634 |
| 2.924 | 1.768 | 0.605 |
| 2.682 | 1.521 | 0.567 |
| 2.224 | 1.299 | 0.584 |
| 1.530 | 0.904 | 0.591 |
| 0 | — | 0.560 |

extrapolated to zero concentration as described previously (19). The intrinsic viscosities in *M* cupriethylenediamine and anhydrous dimethyl sulphoxide were 1.113 and 0.557, respectively.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. C. B. Purves and Dr. A. Taurins for valuable help. One of them (J.K.G.) is also thankful to the Allied Chemical and Dye Corporation for two fellowships and to the Pulp and Paper Research Institute of Canada for two summer stipends.

REFERENCES

1. GILLHAM, J. K. and TIMELL, T. E. *Can. J. Chem.* **36**, 410 (1958).
2. MILKS, J. E. and PURVES, C. B. *J. Am. Chem. Soc.* **78**, 3738 (1956).
3. HAMILTON, J. K. and THOMPSON, N. S. *J. Am. Chem. Soc.* **79**, 6464 (1957).
4. BRASCH, D. J. and WISE, L. E. *Tappi*, **39**, 581, 768 (1956).
5. PAINTER, T. J. Personal communication.
6. BARTH, F. W. and TIMELL, T. E. Unpublished results.
7. BARTH, F. W. and TIMELL, T. E. *Can. J. Chem.* **36**, 1321 (1958).
8. ASPINALL, G. O. and MAHOMED, R. S. *J. Chem. Soc.* 1731 (1954).
9. JONES, J. K. N., MERLER, E., and WISE, L. E. *Can. J. Chem.* **35**, 634 (1957).
10. GORROD, A. R. N. and JONES, J. K. N. *J. Chem. Soc.* 2522 (1954).
11. TIMELL, T. E. Unpublished results.
12. GLAUDEMANS, C. P. J. and TIMELL, T. E. *J. Am. Chem. Soc.* **80**, 941 (1958).
13. TIMELL, T. E. *Tappi*, **40**, 568 (1957).
14. DUTTON, G. G. S. and SMITH, F. *J. Am. Chem. Soc.* **78**, 3744 (1956).
15. TIMELL, T. E., GLAUDEMANS, C. P. J., and CURRIE, A. L. *Anal. Chem.* **28**, 1916 (1956).
16. GLAUDEMANS, C. P. J. and TIMELL, T. E. *J. Am. Chem. Soc.* **80**, 1209 (1958).
17. PAINTER, T. J. Unpublished results.
18. BARTH, F. W. and TIMELL, T. E. *J. Am. Chem. Soc.* (In press).
19. GLAUDEMANS, C. P. J. and TIMELL, T. E. *Svensk Papperstidn.* **61**, 1 (1958).
20. LINDBERG, B. Personal communication.
21. CARSON, J. F. and MACLAY, W. D. *J. Am. Chem. Soc.* **68**, 1015 (1946).
22. HÄGGLUND, E., LINDBERG, B., and MCPHERSON, J. *Acta Chem. Scand.* **10**, 1160 (1956).
23. ADAMS, G. A. *Can. J. Chem.* **35**, 556 (1957).
24. ASPINALL, G. O., HIRST, E. L., and MAHOMED, R. S. *J. Chem. Soc.* 1734 (1954).
25. TIMELL, T. E. and GLAUDEMANS, C. P. J. Unpublished results.
26. JONES, J. K. N. and WISE, L. E. *J. Chem. Soc.* 2750, 3389 (1952).
27. DUTTON, G. G. S. and SMITH, F. *J. Am. Chem. Soc.* **78**, 2505, 3744 (1956).
28. ASPINALL, G. O. and MCKAY, J. E. *J. Chem. Soc.* 1059 (1958).
29. JONES, J. K. N. and PAINTER, T. J. Paper presented at the 133rd meeting of the American Chemical Society, San Francisco, April 1958.
30. ASPINALL, G. O. and CARTER, M. E. *J. Chem. Soc.* 3744 (1956).
31. SAARNIO, J. *Suomen Kemistilehti*, **B**, **29**, 35 (1956).
32. CURRIE, A. L. and TIMELL, T. E. Unpublished results.
33. ANDERSON, E. *J. Biol. Chem.* **165**, 233 (1946).
34. ABDEL-AKHER, M. and SMITH, F. *Nature*, **166**, 1037 (1950).
35. SMITH, F. *J. Chem. Soc.* 2646 (1951).
36. SCHINLE, R. *Ber.* **65**, 315 (1932).
37. FALCONER, E. L. and ADAMS, G. A. *Can. J. Chem.* **34**, 338 (1956).
38. KUHN, R., TRISCHMANN, H., and LÖW, I. *Angew. Chem.* **67**, 32 (1955).
39. FOSTER, A. B. *J. Chem. Soc.* 982 (1953).
40. BOUVENG, H. and LINDBERG, B. *Acta Chem. Scand.* **10**, 1283 (1956).
41. ZIMM, B. H. and MYERSON, I. *J. Am. Chem. Soc.* **68**, 911 (1946).
42. STABIN, J. V. and IMMERGUT, E. H. *J. Polymer Sci.* **14**, 209 (1954).
43. GENUNG, L. B. and MALLAT, R. C. *Ind. Eng. Chem., Anal. Ed.* **15**, 319 (1943).
44. CRAIG, A. W. and HENDERSON, D. A. *J. Polymer Sci.* **19**, 215 (1956).

THE SYSTEM: NICOTINE - METHYLETHYL KETONE - WATER¹

A. N. CAMPBELL, E. M. KARTZMARK, AND W. E. FALCONER²

ABSTRACT

The systems: nicotine-water and nicotine-methylethyl ketone were investigated by thermal analysis but the eutectic points were not obtained due to the extreme viscosity and consequent supercooling of solutions of high nicotine content.

The densities, viscosities, and refractive indices were determined for the nicotine-methylethyl ketone-water system at 25.0° C.

The mutual solubilities of nicotine, methylethyl ketone, and water were determined over the entire temperature range. A ternary critical point was found at 67.3° C, the critical composition being 27 weight per cent nicotine; 14 weight per cent methylethyl ketone.

The methylethyl ketone-water and nicotine-water solubility curves were redetermined. The existing data for the former system were confirmed but the data for the classical system nicotine-water were found to be seriously in error at the higher critical solution temperature. Thus the lower critical solution temperature was found to be 61.5° C, in good agreement with previous figures, but the upper critical solution temperature lies at 233.0° C, some twenty degrees higher than had been obtained by previous workers; the corresponding critical compositions are 36% and 40% nicotine respectively.

INTRODUCTION

The system nicotine-water presents the well-known egg-shaped diagram to be found in almost every textbook of physical chemistry. In other words this system is the classical example of a two-liquid system with both maximum and minimum critical solution temperatures. The system methylethyl ketone-water is similar in character, although the lower critical solution temperature is cut off by the occurrence of the solid phase, ice. It was thought that it would be of interest to investigate the three-component system: nicotine-methylethyl ketone-water, in order to determine the influence of one closed partial miscible region on another of the same type. There existed two main possibilities; either the third component would so increase mutual solubility that the volume of heterogeneity would shrink to a point before meeting the other volume of heterogeneity and thus two volumes of heterogeneity would exist in the solid model, or the two volumes would meet forming a tunnel. A further question was whether, in the latter case, the ternary critical solution temperatures would lie above or below those of the binary systems.

The system methylethyl ketone-water has been investigated by Rothmund (1) and by Marshall (2) but the most recent data are issued by the Shell Chemical Corporation (3). Rothmund found an upper critical solution temperature and he observed the tendency to a lower critical solution temperature but he could not realize it because of the occurrence of ice. Randall and McKenna (4) have determined the freezing curve of this system. The eutectic was found to lie at -88.88° C and the eutectic composition was 99.91 weight per cent methylethyl ketone.

Since our results differ radically (at the higher critical solution temperature) from the accepted data for the system: nicotine-water, it is necessary to deal in some detail with the literature of the subject. This system was first investigated by Hudson (5) in 1904. Neither he nor anyone else has been able to crystallize nicotine; it forms an amorphous solid on cooling. Hence the melting point is unknown.

¹Manuscript received May 10, 1958.

²Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.

³Holder of an N.R.C. Bursary, 1957-58.

Using the method of Alexejew, with solutions sealed in 1 mm diameter capillary tubing and heating in an air bath, Hudson determined the solubility curve for the nicotine-water system and found it to be completely closed. He found both critical compositions to be the same, viz., 32.2 weight per cent nicotine, and that the lower critical solution temperature was 61.0° C and the upper 210° C.

Tsakolotos (6) repeated the work of Hudson in 1909; he found the upper and lower critical temperatures to be 208° C and 60.8° C respectively, and both critical compositions to be 34 weight per cent nicotine. Tsakolotos claimed that the use of extremely pure nicotine did not greatly influence the form of the curve.

Leone (7), in 1926, re-examined the nicotine-water system and obtained results identical with those of Hudson, within one or two degrees. Leone used the method of Alexejew and placed his mixtures in Jena glass tubes which were heated in a double-jacketed paraffin oil bath. He found the upper critical temperature to be 213° C.

EXPERIMENTAL

All chemicals were of the highest purity. Since chemical analysis (of any degree of accuracy) was out of the question, physical analysis was used. Curves representing the behavior of any two physical properties, with respect to composition, make possible the analysis of any mixture, when plotted on a triangular diagram. In order, however, that the method may be accurate, it is necessary that the curves should intersect sharply. With this in mind, we surveyed the field by determining the viscosities, densities, refractive indices (for $H_C = 6563 \text{ \AA}$ and for $H_F = 4861 \text{ \AA}$), and dispersions over the complete composition range of the ternary system. These results are given in Table I. As the result of this survey, we chose the refractive index for hydrogen red light ($\lambda = 6563 \text{ \AA}$) and the density.

Thermal analysis was carried out using a copper-constantan thermocouple and a Brown recording potentiometer. The two-junction thermocouple was calibrated from the freezing points of high purity materials. The available temperature range extended from 0° C to -130° C, with an accuracy of measurement of 0.5° C.

Numerous attempts were made to crystallize pure nicotine, using both slow and rapid cooling, but a glass-like mass was always obtained between -100° C and -120° C. The smooth cooling curve showed no irregularities or breaks. All solutions of water and nicotine containing more than 65 weight per cent nicotine failed to crystallize as did those solutions of methylethyl ketone - nicotine containing more than 50 weight per cent nicotine. Hence, no eutectic was observed in either system. No attempt was made to locate the ternary eutectic, since the binary eutectics were unobtainable. The freezing curve of the methylethyl ketone - water system had been determined previously (4). The freezing-point data are given in Tables II and III.

For the isothermal solubility determinations, three thermostats were used: one for the -11.4° C and 5.0° C isotherms, having a variation of $\pm 0.3^\circ$; one operating at 25.0° C, for the analytical determinations of density and refractive index; and a third, used for all temperatures above 25° C, which had a variation of $\pm 0.2^\circ$ C. The mixtures were made up to approximately known over-all compositions, such that two equilibrium layers of more or less equal volumes would form at the temperature in question. Each layer was sampled, after 24 hours stirring, and analyzed by determining refractive index and density. A cell of heavy-walled glass was used for solutions whose vapor pressure was greater than one atmosphere and the pressure of the vapor was utilized to deliver samples of the top and bottom layers; it was possible to use this cell up to a pressure of twenty atmospheres.

Isotherms of the ternary system were determined at -11.4°C , 5.0°C , 25.0°C , 50.0°C , 65.0°C , 67.5°C , 70.0°C , 85.0°C , 115.0°C , 140.0°C , and 143.0°C and of the nicotine-water conjugate pair at 150.0°C also. The ternary system could not be investigated at 150°C because the pressure was too high. The temperature was controlled to $\pm 0.2^{\circ}\text{C}$ and was measured by a calibrated mercury-in-glass thermometer reading in $1/10^{\circ}$.

The data for all the solubility measurements are listed in Table IV and the isothermal solubility diagrams are shown in Fig. 1 (a and b).

The Alexejew Method

The method of isothermal analysis was abandoned above 143.0°C because the pressure

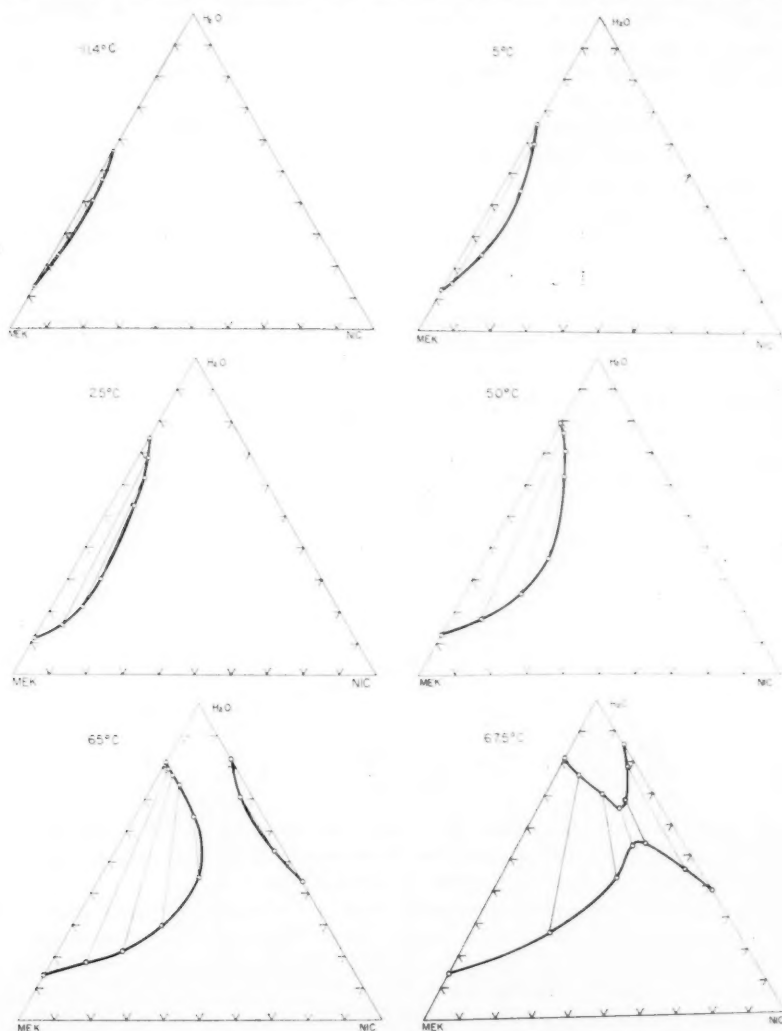


FIG. 1a.

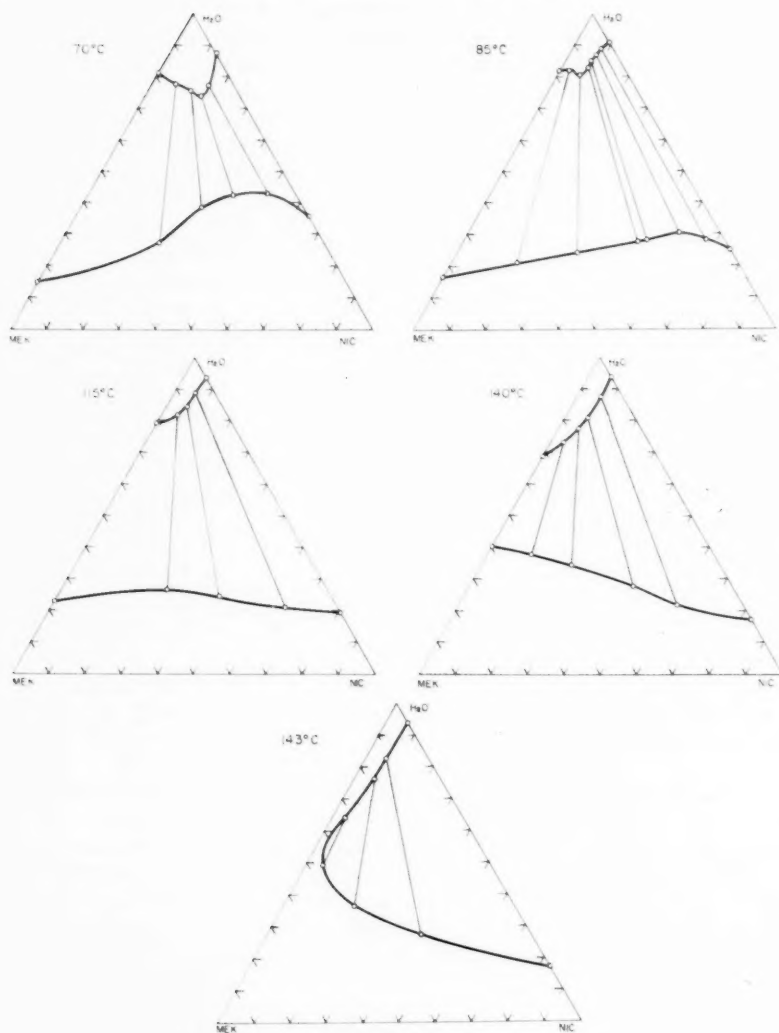


FIG. 1b.

developed made sampling impossible, and resort was made to the Alexejew method to complete the diagram. Our technique is described in complete detail because our results for this region differ so markedly from the accepted figures.

Mixtures of known composition by weight were placed in heavy-walled glass tubes, 8 mm in internal diameter and 12 cm in length. These tubes were filled to approximately two-thirds capacity and then sealed in the blowpipe; the liquid was kept cool to prevent evaporation and composition change during this operation. The tubes were investigated one by one, in a variable temperature bath filled with silicone oil. The temperatures at which homogeneity occurred on heating and that at which heterogeneity occurred on

cooling were noted and the mean temperature taken to be the solution temperature for the composition in question.

The bath was a glass vessel containing two gallons of silicone oil. In the neighborhood of the temperature of homogeneity it was heated at the rate of 1 degree in 5 minutes. The tubes were rotated in the bath by means of a motor and the rate of rotation was varied from 0 to 70 r.p.m. The rotation stirred the contents of the tubes thoroughly, but a speed of rotation greater than 70 r.p.m. developed sufficient centrifugal force to prevent the liquid in the tube flowing freely from end to end.

The temperatures of homogeneity or heterogeneity were measured by a single junction copper-constantan thermocouple. The couple was calibrated against the freezing points of indium (156.5°C), tin (231.9°C), and lead (327.3°C); all the metals were extremely pure. Temperature could be measured to $\pm 0.5^{\circ}\text{C}$. The calibration was repeated after the series of observations was complete but no change in the calibration was observed. As a further check on the reliability of the temperature measurement a sample of pure tin was placed in a tube of the kind used for these measurements and the melting and freezing points determined by the same technique. The mean of these two temperatures agreed, within experimental error, with the literature value for the freezing point of tin.

The tubes were illuminated by a photo spotlight, mounted outside the bath. With this illumination, no difficulty was encountered in observing the condition of the mixture in the tube.

The data from these observations are listed in Table V. Fig. 2 shows temperature versus composition plots for fixed percentages of methylethyl ketone.

Finally, to check the upper critical solution temperature approximately, a few drops of nicotine-water of the upper critical composition were sealed in a piece of heavy-walled capillary tubing of 1 mm internal diameter and 25 mm in length. This was placed in an electrically heated melting-point apparatus and viewed through a magnifying lens. The thermocouple was placed in the opening along with the tube and the top of the opening plugged with asbestos wool. The total volume of the air space surrounding the tube was

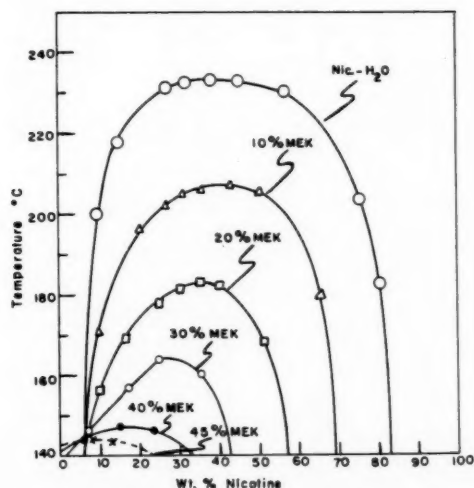


Fig. 2. Temperature versus composition plots with fixed percentages of methylethyl ketone.

between three and four milliliters. Using this apparatus the upper critical solution temperature of the nicotine-water system was found to be $234 \pm 2^\circ \text{C}$.

EXPERIMENTAL RESULTS

TABLE I

PHYSICAL PROPERTIES OF SOLUTIONS OF NICOTINE, METHYLETHYL KETONE, AND WATER AT 25°C

| Composition weight per cent | | | Density g/cm^3 | Relative viscosity | Relative dispersion | Refractive index | |
|--------------------------------|----------|-----|-----------------------------------|-----------------------|------------------------|---------------------------------|---------------------------------|
| Water | Nicotine | MEK | | | | $C, \lambda = 6563 \text{ \AA}$ | $F, \lambda = 4861 \text{ \AA}$ |
| 100 | — | — | 0.99706 | 1.0000 | 1.000 | 1.33066 | 1.33663 |
| 90 | 10 | — | 1.00351 | 1.457 | 0.824 | 1.35046 | 1.35722 |
| 80 | 20 | — | 1.01046 | 2.285 | 0.718 | 1.37127 | 1.37853 |
| 70 | 30 | — | 1.01718 | 3.693 | 0.617 | 1.39217 | 1.40036 |
| 60 | 40 | — | 1.02369 | 5.973 | 0.520 | 1.41290 | 1.42247 |
| 50 | 50 | — | 1.02921 | 9.884 | 0.468 | 1.43497 | 1.44428 |
| 40 | 60 | — | 1.03409 | 16.020 | 0.401 | 1.45649 | 1.46768 |
| 30 | 70 | — | 1.03525 | 23.376 | 0.345 | 1.47536 | 1.48751 |
| 25 | 75 | — | 1.03500 | 26.128 | — | — | — |
| 20 | 80 | — | 1.03169 | 25.819 | 0.292 | 1.49397 | 1.50705 |
| 10 | 90 | — | 1.02173 | 14.369 | 0.242 | 1.50867 | 1.52267 |
| — | 100 | — | 1.00677 | 4.285 | 0.192 | 1.52127 | 1.53606 |
| 90 | — | 10 | 0.98416 | 1.260 | 0.934 | 1.33888 | 1.34491 |
| 80 | — | 20 | 0.97095 | 1.517 | 0.932 | 1.34763 | 1.35287 |
| 8 | — | 92 | 0.82085 | 0.5570 | 0.735 | 1.37632 | 1.38307 |
| — | — | 100 | 0.79979 | 0.4244 | 0.745 | 1.37450 | 1.38115 |
| — | 10 | 90 | 0.81750 | 0.4777 | 0.681 | 1.38670 | 1.39392 |
| — | 20 | 80 | 0.83619 | 0.5487 | 0.642 | 1.40019 | 1.40775 |
| — | 30 | 70 | 0.85454 | 0.6326 | 0.579 | 1.41310 | 1.42140 |
| — | 40 | 60 | 0.87549 | 0.7560 | 0.502 | 1.42582 | 1.43842 |
| — | 50 | 50 | 0.89421 | 0.9089 | 0.449 | 1.44173 | 1.45225 |
| — | 60 | 40 | 0.91636 | 1.129 | 0.390 | 1.46147 | 1.47200 |
| — | 70 | 30 | 0.93655 | 1.412 | 0.335 | 1.47242 | 1.48479 |
| — | 80 | 20 | 0.95868 | 1.882 | 0.300 | 1.48752 | 1.50071 |
| — | 90 | 10 | 0.98181 | 2.696 | 0.239 | 1.50475 | 1.51875 |
| 60 | 10 | 30 | 0.95658 | 2.141 | 0.723 | 1.37411 | 1.38307 |
| 50 | 10 | 40 | 0.93580 | 2.043 | 0.708 | 1.37854 | 1.38565 |
| 40 | 10 | 50 | 0.91412 | 1.824 | 0.698 | 1.38298 | 1.38999 |
| 30 | 10 | 60 | 0.89191 | 1.460 | 0.698 | 1.38590 | 1.39289 |
| 20 | 10 | 70 | 0.86943 | 1.050 | 0.680 | 1.38844 | 1.39542 |
| 10 | 20 | 70 | 0.86477 | 0.8782 | 0.642 | 1.40218 | 1.40968 |
| 70 | 20 | 10 | 0.99595 | 2.669 | 0.684 | 1.37971 | 1.38721 |
| 20 | 30 | 50 | 0.91234 | 1.769 | 0.568 | 1.41622 | 1.42474 |
| 50 | 30 | 20 | 0.98251 | 3.792 | 0.588 | 1.43588 | 1.44434 |
| 20 | 50 | 30 | 0.95795 | 3.740 | 0.462 | 1.44546 | 1.45564 |
| 10 | 80 | 10 | 0.99742 | 7.293 | 0.307 | 1.49284 | 1.50563 |

TABLE II

FREEZING-POINT DATA FOR THE BINARY SYSTEM
NICOTINE-WATER

| Composition weight per cent | | Freezing point, $^\circ \text{C}$ |
|--------------------------------|----------|--------------------------------------|
| Water | Nicotine | |
| 100 | — | 0.00 |
| 90 | 10 | -0.854 ± 0.003 |
| 80 | 20 | -1.455 ± 0.010 |
| 70 | 30 | -2.270 ± 0.010 |
| 60 | 40 | -3.642 ± 0.013 |
| 50 | 50 | -5.9 ± 0.5 |
| 40 | 60 | -12.7 ± 0.5 |
| 35 | 65 | -22.1 ± 0.5 |

TABLE III
FREEZING-POINT DATA FOR THE SYSTEM
NICOTINE-METHYLETHYL KETONE

| Composition weight per cent | | Freezing point, °C |
|--------------------------------|----------|-----------------------|
| MEK | Nicotine | |
| 100 | — | -87.0 ± 0.5 |
| 90 | 10 | -88.3 ± 0.5 |
| 80 | 20 | -89.7 ± 0.5 |
| 70 | 30 | -91.8 ± 0.5 |
| 60 | 40 | -94.0 ± 0.5 |
| 50 | 50 | -99 ± 3 |

TABLE IV
DATA FOR THE ISOTHERMAL SOLUBILITY MEASUREMENTS

| Composition of top layer | | | Composition of bottom layer | | |
|----------------------------|------------|-----------|-----------------------------|------------|-----------|
| Wt. % H ₂ O | Wt. % Nic. | Wt. % MEK | Wt. % H ₂ O | Wt. % Nic. | Wt. % MEK |
| -11.4° C Isotherm | | | | | |
| 13.2 | — | 86.8 | 56.2 | — | 43.8 |
| 19.5 | 1.0 | 79.5 | 47.0 | 1.6 | 51.4 |
| 23.2 | 1.6 | 75.2 | 40.2 | 2.5 | 57.3 |
| Plait point (extrapolated) | | | 30.8 | 2.5 | 65.7 |
| 5.0° C Isotherm | | | | | |
| 13.0 | — | 87.0 | 65.7 | — | 34.3 |
| 15.0 | 2.0 | 83.0 | 59.5 | 2.2 | 38.3 |
| 24.1 | 5.7 | 70.2 | 44.4 | 6.0 | 49.6 |
| Plait point (extrapolated) | | | 33.0 | 7.0 | 60.0 |
| 25.0° C Isotherm | | | | | |
| 11.6 | — | 88.4 | 74.5 | — | 25.5 |
| 15.3 | 5.8 | 78.9 | 68.6 | 2.8 | 28.6 |
| 21.4 | 8.8 | 69.8 | 62.0 | 5.0 | 33.0 |
| 29.9 | 9.2 | 60.9 | 53.2 | 6.5 | 40.3 |
| Plait point (extrapolated) | | | 41.0 | 8.6 | 50.4 |
| 50.0° C Isotherm | | | | | |
| 12.9 | — | 87.1 | 79.4 | — | 20.6 |
| 17.6 | 8.8 | 73.6 | 76.2 | 2.4 | 21.4 |
| 25.4 | 16.0 | 58.6 | 70.6 | 5.8 | 23.6 |
| 36.8 | 17.9 | 45.3 | 62.3 | 9.6 | 28.1 |
| Plait point (extrapolated) | | | 49.3 | 14.6 | 36.1 |
| 65.0° C Isotherm | | | | | |
| 14.2 | — | 85.8 | 81.7 | — | 18.3 |
| 18.4 | 9.5 | 72.1 | 79.4 | 1.8 | 18.8 |
| 21.9 | 17.9 | 60.2 | 77.5 | 3.9 | 18.6 |
| 29.6 | 25.0 | 45.4 | 74.7 | 7.4 | 17.9 |
| 45.0 | 27.5 | 27.5 | 64.4 | 16.2 | 19.4 |
| Plait point (extrapolated) | | | 55.3 | 22.6 | 22.1 |
| 82.4 | 17.6 | — | 43.4 | 56.6 | — |
| 70.4 | 26.0 | 3.6 | 53.0 | 44.3 | 2.7 |
| Plait point (extrapolated) | | | 61.6 | 34.7 | 3.7 |
| 67.5° C Isotherm | | | | | |
| 26.5 | 22.3 | 51.2 | 76.1 | 6.6 | 17.3 |
| 43.4 | 32.8 | 23.8 | 70.0 | 16.0 | 14.0 |
| 53.6 | 32.1 | 14.3 | 65.4 | 22.8 | 11.8 |
| 54.1 | 35.4 | 10.5 | 68.0 | 23.2 | 8.8 |
| 45.7 | 50.5 | 3.8 | 78.4 | 18.9 | 2.7 |
| 70.0° C Isotherm | | | | | |
| 27.0 | 27.3 | 45.7 | 77.5 | 6.5 | 16.0 |
| 38.3 | 33.7 | 28.0 | 75.7 | 11.7 | 12.6 |
| 42.6 | 40.2 | 17.2 | 73.8 | 15.2 | 11.0 |
| 43.0 | 49.4 | 7.6 | 77.1 | 15.6 | 7.3 |
| 87.2 | 12.8 | — | 35.7 | 64.3 | — |

TABLE IV (Concluded)
 DATA FOR THE ISOTHERMAL SOLUBILITY MEASUREMENTS

| Composition of top layer | | | Composition of bottom layer | | |
|----------------------------|------------|-----------|-----------------------------|------------|-----------|
| Wt. % H ₂ O | Wt. % Nic. | Wt. % MEK | Wt. % H ₂ O | Wt. % Nic. | Wt. % MEK |
| 85.0° C Isotherm | | | | | |
| 16.1 | — | 83.9 | 81.4 | — | 18.6 |
| 20.9 | 18.2 | 60.9 | 81.9 | 2.6 | 15.5 |
| 24.0 | 33.7 | 42.3 | 80.4 | 6.4 | 13.2 |
| 27.5 | 48.7 | 23.8 | 82.9 | 7.2 | 9.9 |
| 28.2 | 50.5 | 22.3 | 85.0 | 7.0 | 8.0 |
| 30.3 | 58.7 | 11.0 | 86.6 | 7.7 | 5.7 |
| 28.0 | 67.0 | 5.0 | 88.6 | 8.0 | 3.4 |
| 90.5 | 9.5 | — | 25.0 | 75.0 | — |
| 115.0° C Isotherm | | | | | |
| 23.1 | — | 76.9 | 78.9 | — | 21.1 |
| 26.5 | 29.3 | 44.2 | 81.5 | 4.5 | 14.0 |
| 24.2 | 44.9 | 30.9 | 84.6 | 5.6 | 9.8 |
| 20.7 | 64.9 | 14.4 | 88.8 | 5.5 | 5.7 |
| 19.3 | 80.7 | — | 96.8 | 3.2 | — |
| 140° C Isotherm | | | | | |
| 40.2 | — | 59.8 | 68.3 | — | 31.7 |
| 37.6 | 12.1 | 50.3 | 73.0 | 3.2 | 23.8 |
| 34.2 | 25.0 | 40.8 | 77.5 | 5.5 | 17.0 |
| 27.3 | 45.6 | 27.1 | 85.3 | 5.9 | 8.8 |
| 21.8 | 60.6 | 17.5 | 87.2 | 6.8 | 6.0 |
| 17.0 | 83.0 | — | 93.7 | 6.3 | — |
| 143° C Isotherm | | | | | |
| 27.6 | 42.5 | 29.9 | 82.6 | 6.0 | 11.4 |
| 36.8 | 19.6 | 43.6 | 76.3 | 5.7 | 18.0 |
| 49.1 | 4.9 | 46.0 | 64.0 | 3.7 | 32.3 |
| Plait point (extrapolated) | | | 56.0 | 1.7 | 42.3 |
| Nicotine-water at 62.0° C | | | | | |
| 70 | 30.0 | — | 57.1 | 42.9 | — |
| Nicotine-water at 150.0° C | | | | | |
| 16.8 | 83.2 | — | 94.0 | 6.0 | — |

 TABLE V
 DATA FOR THE ALEXEJEV MEASUREMENTS

| Composition | | | Upper temperature limit of heterogeneous volume, °C |
|-------------|------------------------|------------|-----------------------------------------------------------|
| Wt. % MEK | Wt. % H ₂ O | Wt. % Nic. | |
| — | 20.0 | 80.0 | 183.0±0.5 |
| — | 25.0 | 75.0 | 203.5 |
| — | 32.0 | 68.0 | 219.5 |
| — | 43.0 | 57.0 | 231.0 |
| — | 54.0 | 46.0 | 232.5 |
| — | 62.0 | 38.0 | 233.0 |
| — | 68.0 | 32.0 | 232.5 |
| — | 73.0 | 27.0 | 231.5 |
| — | 85.0 | 15.0 | 218.0 |
| — | 90.0 | 10.0 | 200.0 |
| 10.0 | 25.0 | 65.0 | 180.0 |
| 10.0 | 40.0 | 50.0 | 205.5 |
| 10.0 | 48.0 | 42.0 | 207.0 |
| 10.0 | 55.0 | 35.0 | 205.5 |
| 10.0 | 59.0 | 31.0 | 205.0 |
| 10.0 | 63.0 | 27.0 | 202.0 |
| 10.0 | 70.0 | 20.0 | 196.0 |
| 10.0 | 80.0 | 10.0 | 171.0 |
| 20.0 | 29.0 | 51.0 | 168.5 |
| 20.0 | 40.0 | 40.0 | 182.5 |
| 20.0 | 45.0 | 35.0 | 183.0 |
| 20.0 | 50.0 | 30.0 | 181.0 |
| 20.0 | 55.0 | 25.0 | 178.0 |

TABLE V (Concluded)
 DATA FOR THE ALEXEJEW MEASUREMENTS

| Composition | | | Upper temperature limit of heterogeneous volume, °C |
|-------------|------------------------|------------|-----------------------------------------------------------|
| Wt. % MEK | Wt. % H ₂ O | Wt. % Nic. | |
| 20.0 | 63.0 | 17.0 | 169.5 |
| 20.0 | 70.0 | 10.0 | 156.0 |
| 30.0 | 35.0 | 35.0 | 159.5 |
| 30.0 | 45.0 | 25.0 | 163.0 |
| 30.0 | 52.0 | 18.0 | 157.0 |
| 30.0 | 63.0 | 7.0 | 146.0 |
| 40.0 | 37.0 | 23.0 | 146.5 |
| 40.0 | 45.0 | 15.0 | 147.5 |
| 40.0 | 50.0 | 10.0 | 145.5 |
| 40.0* | 55.0 | 5.0 | 143.5 |
| 45.0 | 42.0 | 13.0 | 143.5 |
| 45.0* | 47.0 | 8.0 | 144.5 |

*These samples were made up by direct weighing, as they were heterogeneous at room temperature.

 TABLE VI
 DATA FOR THE MUTUAL SOLUBILITIES OF THE METHYLETHYL
 KETONE-WATER SYSTEM

| Temperature, °C | Composition of top layer | | Composition of bottom layer | |
|--------------------|-----------------------------|-----------|--------------------------------|-----------|
| | Wt. % H ₂ O | Wt. % MEK | Wt. % H ₂ O | Wt. % MEK |
| -11.4 | 13.2 | 86.8 | 56.2 | 43.8 |
| 5.0 | 13.0 | 87.0 | 65.7 | 34.3 |
| 25.0 | 11.6 | 88.4 | 74.5 | 25.5 |
| 50.0 | 12.9 | 87.1 | 79.4 | 20.6 |
| 65.0 | 14.2 | 85.8 | 81.7 | 18.3 |
| 85.0 | 16.1 | 83.9 | 81.4 | 18.6 |
| 115.0 | 23.1 | 76.9 | 78.9 | 21.1 |
| 140.0 | 40.2 | 59.8 | 68.3 | 31.7 |
| 142.6 (CRIT.) | 55.0 | 45.0 | 55.0 | 45.0 |

DISCUSSION OF RESULTS

The Binary System: Methylene Ketone - Water

At 25° C, methylethyl ketone and water are not completely miscible. Hence, the physical properties investigated, viz., density, viscosity, refractive index, and dispersion, were limited to the completely intersoluble region. The freezing-point curve of this system was not determined.

Our results for the mutual solubility of these two liquids above 0° C are in close agreement with the results of Marshall (2) and of the Shell Laboratories (3); they disagree with the earlier work of Rothmund (1). The upper critical solution temperature was found to be 142.6° C and the critical composition 45% by weight methylethyl ketone.

The lower critical solution temperature could not be obtained; at temperatures below -12° C crystallization of ice occurred though previous workers claim to have supercooled to -20° C. Our results for the solubility of water in methylethyl ketone are in exact agreement with those of Randall and McKenna (4) but our results for the solubility of methylethyl ketone in water appear to be slightly greater.

We estimate that the lower critical solution temperature, if it were realizable, would lie about -35° C and the critical composition would be about 75 weight per cent methylethyl ketone. The data for the mutual solubilities of the methylethyl ketone-water system are given in Table VI.

The Binary System: Nicotine-Water

The physical properties, density, viscosity, and refractive indices, were investigated at 10% intervals, from 0 to 100% nicotine. A maximum density was observed at 70 weight per cent nicotine and a maximum viscosity at 77% nicotine. The graphs of refractive index against composition were straight lines. The density inversion at 90° C, observed by Hudson (5), was confirmed; the water-rich layer became heavier than the nicotine-rich layer about this temperature. We estimate that the eutectic composition, if the eutectic were realizable, would be about 75 to 80% nicotine, but the measurements could not be pushed beyond 65 weight per cent.

The results for mutual solubility by the isothermal analysis method varied slightly from previous measurements and tended to flatten the lower part of the solubility curve somewhat. The so-called "rectilinear diameter" was plotted (Fig. 3). The lower critical temperature was found to be $61.5 \pm 0.2^\circ \text{C}$ and the lower critical composition 36 weight per cent nicotine.

The upper half of the solubility curve differs considerably from previous results. Identical solution temperatures were obtained, independently of whether the nicotine

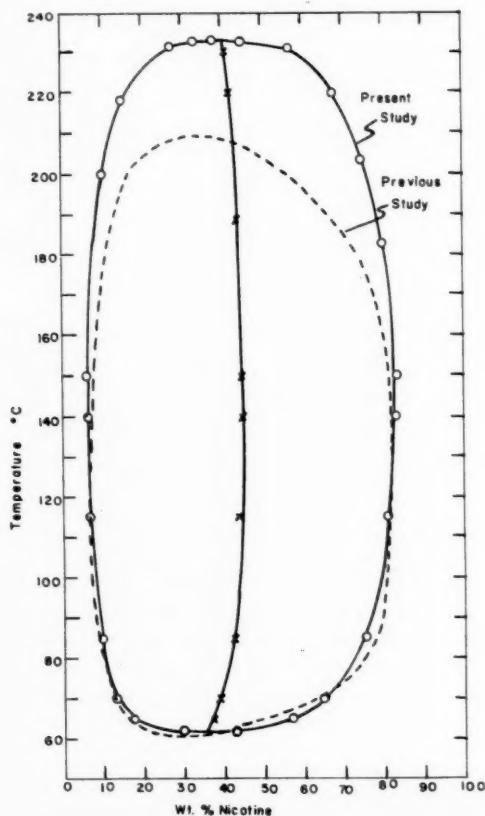


FIG. 3. Nicotine-water mutual solubility diagram.

used was old or new, freshly redistilled or not. The upper critical temperature was found to be $233.0 \pm 0.5^\circ \text{C}$, 20° higher than had previously been reported (5, 6, 7). The upper critical composition is 40% nicotine. The data for the mutual solubilities of the nicotine-water systems are given in Table VII and plotted in Fig. 3.

TABLE VII
DATA FOR THE MUTUAL SOLUBILITIES OF THE NICOTINE-WATER SYSTEM

| Temperature, $^\circ \text{C}$ | Composition of top layer | | Composition of bottom layer | |
|-----------------------------------|-----------------------------|------------|--------------------------------|------------|
| | Wt. % H_2O | Wt. % Nic. | Wt. % H_2O | Wt. % Nic. |
| 61.5 (CRIT.) | 64.0 | 36.0 | 64.0 | 36.0 |
| 62.0 | 70.0 | 30.0 | 57.1 | 42.9 |
| 65.0 | 82.4 | 17.6 | 43.4 | 56.6 |
| 70.0 | 87.2 | 12.8 | 35.7 | 64.3 |
| 85.0 | 90.5 | 9.5 | 25.0 | 75.0 |
| 115.0 | 19.3 | 80.7 | 96.8 | 3.2 |
| 140.0 | 17.0 | 83.0 | 93.7 | 6.3 |
| 150.0 | 16.8 | 83.2 | 94.0 | 6.0 |

| Composition | | Upper temperature limit of heterogeneous area, $^\circ \text{C}$ |
|----------------------------|------------|------------------------------------------------------------------------|
| Wt. % H_2O | Wt. % Nic. | |
| 20.0 | 80.0 | 183.0 ± 0.5 |
| 25.0 | 75.0 | 203.5 |
| 32.0 | 68.0 | 219.5 |
| 43.0 | 57.0 | 231.0 |
| 54.0 | 46.0 | 232.5 |
| 60.0 (CRIT.) | 40.0 | 233.0 |
| 62.0 | 38.0 | 233.0 |
| 68.0 | 32.0 | 232.5 |
| 73.0 | 27.0 | 231.5 |
| 85.0 | 15.0 | 218.0 |
| 90.0 | 10.0 | 200.0 |

The Binary System: Methyleneethyl Ketone - Nicotine

Methyleneethyl ketone and nicotine are intersoluble at all temperatures. The densities, viscosities, and refractive indices were determined at intervals of 10% by weight. The graphs of these properties versus composition at 25°C are very nearly linear, with the exception of the viscosity curve whose slope begins to increase at a concentration of 50% nicotine, and continues to increase to a maximum at pure nicotine. The freezing curve shows no marked change of slope and therefore it is impossible to estimate the eutectic temperature and composition.

The Ternary System: Methyleneethyl Ketone - Nicotine - Water

At 25°C , these three substances are completely miscible except for a small region with a composition of less than 9% nicotine, and between 25 and 88% ketone. A picture of the solid model representing composition versus temperature can be visualized by imagining the isotherms of Fig. 1 to be placed vertically above one another at the appropriate distances. When this is done, a tunnel-shaped solid results. The upper part of this tunnel forms a smooth surface running from the upper critical solution temperature of the methyleneethyl ketone-water system to the upper critical solution temperature of the nicotine-water system, but, on the lower surface, a maximum occurs in the homogeneous volume, that is, a ternary critical solution point exists. The solubility surface rises from

the ice line of the methylethyl ketone - water system and meets a surface rising continuously from the lower critical solution temperature of the nicotine-water system. The maximum of this dent in the surface lies at a temperature of $67.3 \pm 0.2^\circ \text{C}$ and at a composition of 27 weight per cent nicotine, and 14 weight per cent methylethyl ketone. If a corresponding critical point exists on the upper surface of the solubility model, the critical solution must contain so little nicotine, less than say one per cent, as to be non-detectable by our methods. The data for the ternary system (by the Alexejew method) are given in Table V.

Obviously, none of the systems was studied isobarically, but under the vapor pressure of the system which may be as great as twenty atmospheres. The question of what the data would be under a constant pressure of 1 atmosphere is meaningless, since the systems would cease to exist (they would vaporize completely) under this pressure.

REFERENCES

1. ROTHMUND, V. *Z. physik. Chem.* **26**, 433 (1898).
2. MARSHALL, A. *J. Chem. Soc.* **89**, 1350 (1906).
3. SHELL CHEMICAL CORPORATION. *Methylethyl ketone*. 1950. p. 65-67.
4. RANDALL, M. and MCKENNA, F. E. *J. Am. Chem. Soc.* **73**, 4859 (1951).
5. HUDSON, C. S. *Z. physik. Chem.* **47**, 113 (1904).
6. TSAKOLOTOS, M. D. E. *Bull. soc. chim. France*, **5**, 397 (1909).
7. LEONE, P. *Atti congr. nazl. chim. pura ed appl.* 2nd Congr. 1209 (1926).

THE DETERMINATION OF UO_3 AND U_3O_8 IN BROWN OXIDE¹

L. G. STONHILL

ABSTRACT

Investigations leading to a method for the analysis of mixtures of the oxides UO_3 , U_3O_8 , and UO_2 are described.

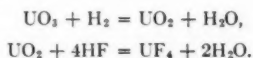
Uranic oxide is extracted with hot ammonium citrate solution, uranic and uranous-uranic oxides are determined together by solution in phosphoric acid followed by titration of U(VI) with titanous sulphate, and uranous oxide found by difference.

INTRODUCTION

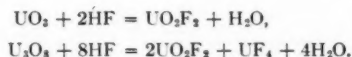
"Brown oxide" is a product consisting essentially of uranium dioxide, but with a molecular formula UO_{2+x} , where x is zero in the case of high purity brown oxide and will have larger values if oxygen is present in excess over the proportion required to form the dioxide.

It is important as an intermediate stage between refined UO_3 and uranium tetrafluoride ("green salt") in the production of uranium metal, and in addition, interest is developing in its use in reactor fuel elements without further processing.

In the Port Hope, Ontario, plant of Eldorado Mining and Refining Limited, "brown oxide" is produced by hydrogen reduction of UO_3 and then hydrofluorinated to "green salt" according to the reactions:



Owing to the difficulty of achieving complete reduction to UO_2 under plant conditions, a certain amount of U(VI) may remain in the "brown oxide" and will give uranyl fluoride by the reactions:



Therefore, as the uranyl fluoride content of "green salt" must be kept low, it is essential for control purposes to know the proportion of the higher oxides UO_3 and U_3O_8 in the "brown oxide" intended for its production; the research reported here was undertaken to provide such data.

It will be assumed in what follows that uranium is present in "brown oxide" only in the valencies IV and VI and the forms UO_2 , U_3O_8 , and UO_3 . In the case of certain poorly reduced samples the author has made thermogravimetric observations which tend to support the latter assumption.

EXPERIMENTAL

1. Determination of UO_3

The loss in weight of a brown oxide sample after a 15-minute extraction with refluxing ammonium citrate solution is a method current in the industry for the estimation of UO_3 contents (1).

Under such conditions, however, U_3O_8 is markedly soluble and a source of error is thereby introduced. In the hope of overcoming this objection, qualitative tests were

¹Manuscript received May 20, 1958.

Contribution from the Metallurgical Laboratories, Eldorado Mining and Refining Ltd., Ottawa, Canada.

made upon each of the three oxides with possible alternative complexants, listed in Table I. UO_3 dissolved fairly rapidly in cold solutions of some, but in other cases the application of heat was necessary; rapid dissolution then occurred.

UO_2 , reduced at 500° in a mixture of hydrogen and nitrogen to simulate plant conditions, then ground to pass a 325-mesh screen, resisted the action of all the reagents under the conditions of the method described in section 4.1, and after 2 hours cold extraction (series A) or 15 minutes refluxing (series B) no dissolved uranium could be detected by the well-known peroxide test.

U_3O_8 , prepared by igniting UO_2 in air at 500° followed by grinding to pass a 325-mesh screen, was detectably soluble in each reagent, and quantitative data on this solubility, obtained using the same conditions as for the UO_2 tests, are recorded in Table I. It should be noted that these are not equilibrium values but provide a comparative basis for selecting the reagent with least effect on U_3O_8 .

TABLE I
SOLVENT ACTION OF VARIOUS REAGENTS ON U_3O_8

| Reagent | Weight of U_3O_8 dissolved per 100 ml of reagent solution |
|---------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Series A: Reaction with UO_3 fast in cold solution | |
| Hydrazine sulphate 5% w/v | 10 mg |
| Oxalic acid 5% w/v | 10 |
| Sulphuric acid 2% v/v | 6 |
| Sulphosalicylic acid 5% w/v | 4 |
| Series B: Reaction with UO_3 fast in boiling solution (all solutions 5% w/v) | |
| Ammonium oxalate | 18 |
| Ammonium malonate | 20 |
| Ammonium succinate | 19 |
| EDTA | 14 |
| Ammonium tartrate | 8.5 |
| Ammonium citrate | 8.3 |

Clearly, absolute specificity to UO_3 cannot be attained with the reagents so far suggested, but, of series A, sulphosalicylic and weak sulphuric acids might be of practical use, also ammonium citrate and tartrate of series B. All four are an improvement upon ammonium oxalate, and the latter's homologues, malonate and succinate, need not be further considered.

The reproducibility of results obtained using sulphosalicylic and weak sulphuric acids was found to be poor, apparently owing to their strong retention by UO_2 , an effect noted elsewhere with potassium oxalate (2). On the other hand, ammonium citrate and tartrate both gave results which were reproducible and in agreement with each other within the limits of error associated with gravimetric procedures. Of this pair, ammonium citrate has been chosen for routine work but appears to have no special advantage over tartrate.

As the data in Table I imply, a 100%-pure U_3O_8 sample would be soluble to the extent of about 1.7% in both tartrate and citrate solutions under experimental conditions, but since brown oxide of good production quality contains only a few per cent U_3O_8 , the latter's dissolution tendency may be expected to have no serious effect on the UO_3 values obtained in practice.

Regarding the preparation of samples for UO_3 determination, it has been found that

grinding beyond the stage at which the whole sample has been reduced below 325-mesh screen size does not significantly increase the proportion dissolved by ammonium citrate solution. Excessive grinding will in fact tend to increase the rate at which the contained U_3O_8 reacts, and should be avoided.

2. Determination of U_3O_8

For practical purposes, U_3O_8 is conveniently regarded as uranous-uranic oxide ($UO_2 \cdot 2UO_3$). Provided that it can be dissolved to give a mixture of U(VI) and U(IV) in the proportion of 2:1 expected from this formula, analysis of the resulting solution for either U(VI) or U(IV) would be a suitable method for its determination. In the present context, with both UO_3 and UO_2 also present, allowance must be made for a contribution to the quantity of both valency states arising from these other oxides because U_3O_8 cannot be specifically extracted from admixture. UO_3 present as such can be determined alone (as has been seen above) and therefore analysis of a solution of the mixed oxides for U(VI), with a correction for UO_3 , would establish the amount of U_3O_8 present.

The experimental investigation was directed firstly towards a method for determining U(VI) in presence of U(IV), secondly to procedures for dissolving the mixed oxides without change in the proportions of each valency state, and finally to showing that U_3O_8 can in fact be determined in accordance with the foregoing discussion.

2.1 The Determination of U(VI)

It was quickly established that U(VI) cannot be determined spectrophotometrically in presence of U(IV). The main absorbance regions of equal concentrations of both valency states of uranium in sulphuric acid over the range of the Beckman DU instrument are such that U(VI) has no absorption wave-length unaffected by the presence of U(IV).

Attention was therefore transferred to volumetric methods. Consideration of the relevant oxidation-reduction potentials showed that either Ti(III) or Cr(III) should be suitable titrants for U(VI). Of the two, the more strongly reducing chromous ion has the operating disadvantage of instability in storage unless prepared in a highly purified state, and potentiometric titration with titanous sulphate was decided on.

The reduction of U(VI) by Ti(III) is slow at ordinary temperatures and low acidity, and in the titration of UO_3 dissolved in either hydrochloric, sulphuric, or phosphoric acids it was found necessary to increase both factors to speed up the reaction. At 80° C, and with an acid concentration of 50%, a satisfactorily sharp inflection of potential versus titrant volume was found to occur. As is usual in this type of titration (3) the addition of an ion with an intermediate redox potential to the solution being titrated speeded the attainment of a steady potential after each addition of titrant; ferrous sulphate was found satisfactory. Alternatively ammonium oxalate or citrate (4) may be used.

2.2 Dissolution of U_3O_8

While UO_3 dissolves rapidly in strong acids, U_3O_8 is rather more resistant and requires the application of heat. Phosphoric acid was found suitable as a solvent for all three oxides and is used in the recommended analytical procedure. At an early stage in these experiments it was obvious that air had to be completely excluded from hot solutions of U(IV) otherwise oxidation occurred, and special precautions were taken to ensure this. Air-free phosphoric acid was used for dissolution of the oxides, and both dissolution and titration stages were carried out in the same vessel, which was kept full of carbon dioxide throughout the analytical operations.

2.3 Stoichiometry of U_3O_8

To demonstrate that U_3O_8 does in fact dissolve in phosphoric acid giving the ratio of U(VI) to U(IV) expected from the formula ($UO_2 \cdot 2UO_3$), weighed quantities of pure U_3O_8 were dissolved in phosphoric acid and titrated with a titanous sulphate solution previously standardized with pure UO_3 . Within the usual limits of experimental error, the ratio of U(VI) to total uranium content was in each case found to be 2:3.

3. Determination of UO_2

It is not possible to extract UO_2 specifically from a mixture of oxides, and an approach via a U(IV) determination would, in the presence of U_3O_8 , have little value. The UO_2 content of a mixture is for present purposes, therefore, taken as the difference from 100% of the sum of the UO_3 and U_3O_8 contents. An independent method involving thermogravimetric oxidation of the UO_2 will form the subject of a later communication.

In spite of the wide variation in composition between these samples, the concordance between total uranium values obtained by independent methods is satisfactory, and particularly so in the cases of samples A, H, and J (see Table II), where the directly assayed components constitute the major fraction of the whole, and where, consequently, analytical errors would have the largest effect on the total uranium value.

4. Analytical Procedures

1. Determination of UO_3

Reagent required: dibasic ammonium citrate.

The part of the sample used for the UO_3 determination should completely pass a 325-mesh sieve. Reflux an accurately weighed quantity, about 0.5 g, with 200 ml 5% ammonium citrate solution for 15 minutes. Recover the residue by filtration through a sintered-glass filter crucible under suction; wash with hot water, followed by acetone, and dry at 80°C for 1 hour. Determine the loss in weight of the original sample. This represents its UO_3 content.

2. Determination of U_3O_8

The apparatus required is depicted in Fig. 1. Reagents required:

(a) Phosphoric acid 50% v/v, air-free. This solution is freed from oxygen by passing in a stream of pure nitrogen or carbon dioxide.

(b) Pure U_3O_8 . Ignite U_3O_8 , UO_3 , or UO_2 in air at 750°C for 1 hour. One gram of U_3O_8 is equivalent to 0.6793 g UO_3 when its solution is used for the standardization of titanous sulphate solution.

(c) Titanous sulphate solution. Dilute the commercial 15% titanous sulphate solution in the ratio 1:8 with 4 *N* sulphuric acid, and store in an aspirator bottle attached to a hydrogen generator. After the solution has been left standing for 2 days, standardize it with pure U_3O_8 , following the titration procedure below.

(d) Ferrous ammonium sulphate, reagent grade.

The procedure is as follows: Weigh accurately a quantity of powdered brown oxide containing about 200 mg U(VI) as UO_3 . Add this to 50 ml air-free 50% phosphoric acid in a 500-ml three-necked flask and swirl gently to mix. Pass CO_2 into the flask at this stage and throughout the subsequent procedure to prevent entry of oxygen. Heat to boiling, and allow the acid to concentrate until a clear solution is obtained. Cool somewhat, add 150 ml more air-free 50% phosphoric acid and a glass-covered magnetic stirring bar, heat to 80–85°C, add 0.25 g ferrous ammonium sulphate, and titrate potentiometrically with the standard titanous sulphate solution, stirring continuously. The result is the U(VI) content of the sample expressed as total equivalent UO_3 ; subtraction of the percentage of UO_3 found to be present as such by ammonium oxalate extraction

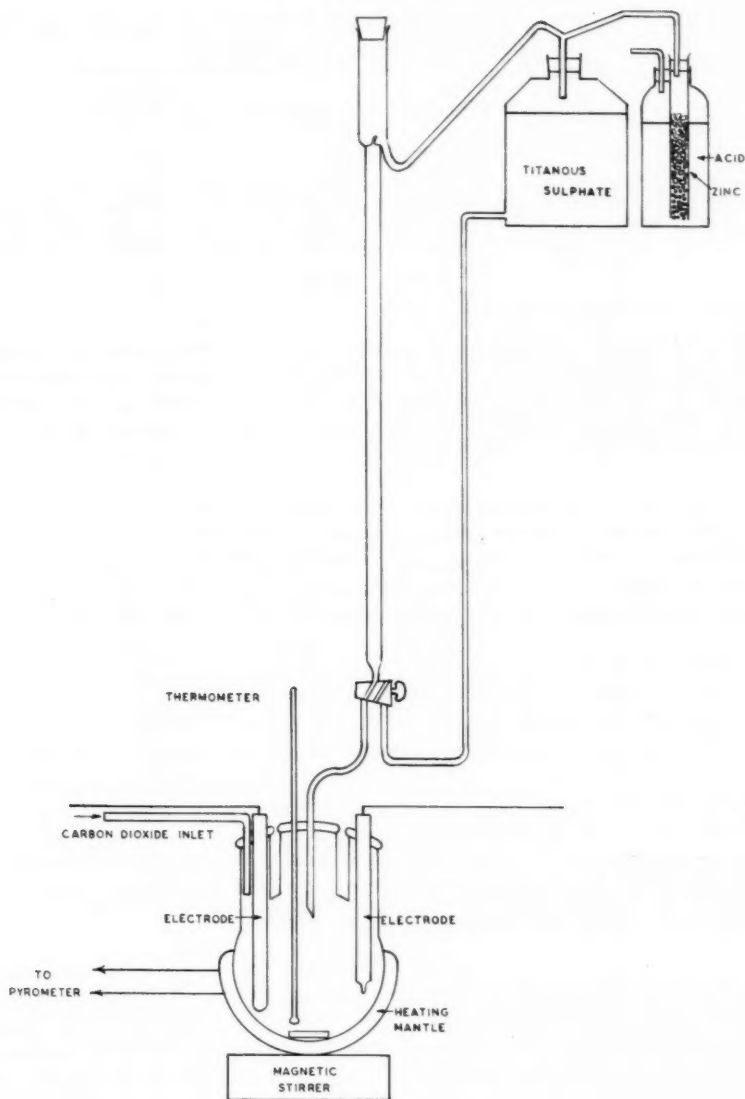


FIG. 1.

gives the percentage of the sample which is UO_3 present in U_3O_8 ; and the product of that figure and the factor 1.4717 is the percentage of actual U_3O_8 in the sample.

RESULTS

To test, over as wide a range of mixtures as possible, the performance of the analytical method resulting from the investigations described above, a series of brown oxide specimens of varying quality was assayed and a few of the results are shown in Table II.

TABLE II
RESULTS OF BROWN OXIDE ASSAYS

| Sample | % UO_2 | % U_2O_5 | % UO_2 by difference |
|--------|-----------------|--------------------------|----------------------------------|
| A | 4.75 | 54.1 | 41.2 |
| B | 4.82 | 15.1 | 80.1 |
| C | 16.4 | 18.5 | 65.1 |
| D | 0.86 | 4.52 | 94.62 |
| E | 1.63 | 6.78 | 91.59 |
| F | 1.02 | 6.33 | 92.65 |
| G | 3.60 | 7.95 | 88.45 |
| H | 3.11 | 70.3 | 26.6 |
| J | 2.17 | 64.2 | 33.6 |

There is at present no alternative method for determining individual oxides in a mixture for comparison with the above results, but it is of interest to compare the total uranium content of each sample calculated from the results of the present method with that given by standard methods. The comparison is given in Table III.

TABLE III
COMPARISON OF TOTAL URANIUM VALUES

| Sample | % Uranium as given by: | | |
|--------|------------------------|--------------------------------------|--------------------------|
| | Present method | Conversion to U_2O_5 | Differential colorimetry |
| A | 86.10 | 85.89 | 86.04 |
| B | 87.41 | 87.21 | 87.25 |
| C | 86.73 | 86.46 | 86.32 |
| D | 87.96 | 87.65 | 87.97 |
| E | 87.85 | 87.74 | 87.82 |
| F | 87.89 | 87.70 | 87.52 |
| G | 87.71 | 87.70 | 87.70 |
| H | 85.65 | 85.41 | 85.45 |
| J | 85.90 | 85.87 | 85.90 |

REFERENCES

1. UNPUBLISHED METHOD.
2. U.S. ATOMIC ENERGY COMM. A-2912, **3**, 49 (1946).
3. KOLTHOFF, I. M. and LIVINGSTON, R. S. Ind. Eng. Chem., Anal. Ed. **7**, 209 (1935).
4. EL-SHAMY, H. F. and ZAYAN, S. EL-DIN. Analyst, **80**, 65 (1955).

THE GAS PHASE REACTIONS OF PERFLUORO-*n*-PROPYL RADICALS WITH METHANE AND ETHANE¹

G. GIACOMETTI² AND E. W. R. STEACIE

ABSTRACT

The rate constants and activation energies for the reactions of C_3F_7 radicals with methane and ethane have been measured by photolyzing mixtures of $C_3F_7COC_3F_7$ and hydrocarbon with 3130 Å light. Photolysis of mixtures of the ketone, methane, and deuterium has been used to check previous measurements on the reaction of C_3F_7 and deuterium.

INTRODUCTION

The availability of completely fluorinated alkyl radicals obtained via a very simple mechanism from the photolysis of the corresponding ketones (1, 2) makes it worth while to study their reactions with simple hydrocarbons or other substrates, with the object of throwing further light on the effect of the structure of the reactants on the rate constants. The mechanism of production of n - C_3F_7 radicals from perfluoro di- n -propyl ketone has been investigated (2) and their reactions with hydrogen and deuterium have been subsequently studied (3).

While the mechanism of the photolysis is extremely simple in this case, especially compared with the non-fluorinated compound, there is one analytical feature of this system which complicates the situation. Owing to the very similar volatilities of the perfluoro di- n -propyl ketone and of the perfluoro- n -hexane, it is impossible to separate the latter from the bulk of the unreacted material by the usual low-temperature distillation technique.

This difficulty can be overcome, however, by taking advantage of the simplicity of the mechanism and estimating the hexane by a stoichiometric balance. This was done previously in the reaction of n - C_3F_7 with hydrogen and deuterium, although in this case some uncertainty affected the results because of ignorance of the fate of the hydrogen atoms produced in the system (3).

In this paper we present the analogous results obtained for the reactions of C_3F_7 radicals with ethane and methane, which are not affected by such a complication. This circumstance also permits an independent determination of the hydrogen reaction rate by performing experiments in the presence of both methane and deuterium.

EXPERIMENTAL

Apparatus

The apparatus was essentially the same as that used in the experiments on the hydrogen reaction. The light source was a B.T.H. high-pressure mercury lamp (ME/D, 250 watts) operated on stabilized 220 v d-c. The 3130 Å radiation was isolated by a standard set of filters. The quartz reaction cell was 10 cm long and had a capacity of 175 cc; it was fully illuminated by the parallel beam of light. The cell was maintained at the desired temperature by an aluminum block furnace and the temperature was constant to $\pm 1^\circ C$.

The filling system was of a conventional type as was the analytical line which consisted of two Ward-LeRoy stills, one solid nitrogen trap, a small mercury diffusion pump, a

¹Manuscript received July 27, 1958.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.

Issued as N.R.C. No. 4912.

²National Research Council Postdoctorate Fellow 1956-58. Present address: Istituto di Chimica Fisica, Università di Padova, Padova, Italy.

gas burette, and a Toepler pump for sample collection. A small CuO furnace, operating at 250° C, could also be inserted in the line when necessary. All stopcocks were avoided by use of appropriate mercury cutoffs.

Materials

The ketone was supplied by Dr. L. C. Leitch of these laboratories and its purity checked by careful distillation in a Podbielniak column (b.p. 75° C) and by mass spectrometry. Deuterium was obtained from a Stuart Oxygen Company cylinder and was passed through hot palladium before storage in a 5-liter bulb connected to the line. Mass spectroscopic analysis gave a D content of 95.4% and all results have been corrected accordingly. Methane and ethane were research grade Philips products and were carefully checked for impurities in the mass spectrometer.

Procedure

After the ketone had been introduced into the cell, its pressure was measured with a constant-volume manometer. The ketone was then frozen out at liquid nitrogen temperature and methane or ethane was introduced at the desired pressure. The two reactants were then mixed by expanding them a few times by means of a Toepler pump. The total gas pressure was always measured as a further check. When deuterium was also present, the relative amount of the two gases was measured by reading their pressures in two separate sections of the apparatus whose volume ratio had been previously measured.

The photolysis was allowed to proceed up to 4 to 6% decomposition of the ketone. The analyses were carried out by the usual technique of low-temperature fractionation and mass spectrometry.

In the methane experiments the products of the photolysis were CO, C₃F₇H, C₄F₇H₃, C₂H₆, and C₆F₁₄. The first fraction was collected at -210° C and it contained all the CO together with large quantities of methane. The CO was then separated by oxidation in the CuO furnace and measured in the gas burette. Blank experiments showed that no methane was oxidized during the short time of the operation. After pumping off all the remaining methane and possible traces of ethane, a second fraction was collected at -105° C containing all the C₃F₇H and the C₄F₇H₃. The C₃F₇H content was estimated by the peak at mass 51 of its mass spectrum. The C₄F₇H₃ was estimated by difference and the main peaks of the mass spectrum of this compound are shown in Table I.

In the ethane experiments the products were CO, C₃F₇H, C₅F₇H₅, *n*-C₄H₁₀, and C₆F₁₄. CO was collected at -210° C and a few checks by oxidation in the CuO furnace showed that it did not contain ethane. Ethane was removed at -155° C. The fraction at

TABLE I
MASS SPECTRUM OF *n*-C₃F₇CH₃ (MAIN OR CHARACTERISTIC PEAKS)

| Mass <i>m</i> | Relative height | Probable ion |
|---------------|-----------------|------------------------------------------------------------|
| 169 | 5.6 | C ₃ F ₇ ⁺ |
| 119 | 3.1 | C ₂ F ₅ ⁺ |
| 115 | 1.4 | C ₂ F ₄ CH ₃ ⁺ |
| 96 | 6.1 | C ₂ F ₃ CH ₃ ⁺ |
| 77 | 6.0 | C ₂ F ₂ CH ₃ ⁺ |
| 69 | 5.1 | CF ₃ ⁺ |
| 65 | 100.0 | CF ₂ CH ₃ ⁺ |
| 64 | 3.4 | CF ₂ CH ₂ ⁺ |
| 45 | 12.9 | CFCH ₂ ⁺ |

-105°C contained all the $\text{C}_3\text{F}_7\text{H}$, part of the $\text{C}_3\text{F}_7\text{H}_5$, and all the *n*-butane. A further fraction at -90°C contained only $\text{C}_3\text{F}_7\text{H}_5$. The mass spectrum of this compound is shown in Table II. The peak used for the analysis was the large 79 peak which does not occur with $\text{C}_3\text{F}_7\text{H}$, *n*-butane, or the ketone.

TABLE II
MASS SPECTRUM OF $\text{C}_3\text{F}_7\text{C}_2\text{H}_5$ (MAIN OR CHARACTERISTIC PEAKS)

| Mass <i>n</i> | Relative height | Probable ion |
|---------------|-----------------|----------------------------------------------|
| 169 | 27.9 | C_3F_7^+ |
| 159 | 6.4 | $\text{C}_3\text{F}_5\text{C}_2\text{H}_4^+$ |
| 119 | 20.1 | C_3F_5^+ |
| 109 | 12.2 | $\text{C}_3\text{F}_3\text{C}_2\text{H}_4^+$ |
| 95 | 8.4 | $\text{C}_3\text{F}_3\text{CH}_2^+$ |
| 89 | 3.2 | $\text{C}_3\text{F}_3\text{C}_2\text{H}_3^+$ |
| 79 | 100 | $\text{CF}_2\text{C}_2\text{H}_5^+$ |
| 77 | 12.9 | $\text{CF}_2\text{C}_2\text{H}_3^+$ |
| 69 | 75.1 | CF_2^+ |
| 59 | 32.1 | CFC_2H_4^+ |

The experiments with methane and deuterium were carried out in a manner completely analogous to that used by Miller and Steacie (3) with mixtures of hydrogen and deuterium. The peaks at mass 51 and 52 were used to measure the ratio of $\text{C}_3\text{F}_7\text{H}$ to $\text{C}_3\text{F}_7\text{D}$ and blank runs were performed before each experiment to check the ratio in the absence of hydrogen.

RESULTS

The results for the three sets of experiments are summarized in Tables III, IV, and V. A few runs were performed at quite different light intensities and showed that the results were independent of such changes.

TABLE III
THE REACTION OF *n*- C_3F_7 RADICAL WITH METHANE

| Temp., $^{\circ}\text{K}$ | Reactants | | Products | | Time, sec | $\text{cc}^{\frac{1}{2}} \frac{k_3/k_2^{\frac{1}{2}}}{\text{molecule}^{-\frac{1}{2}} \text{sec}^{-\frac{1}{2}}} \times 10^{13}$ |
|------------------------------|---------------------------|----------------------------------|---------------------------------------|----------------------------------------------------------|--------------|---------------------------------------------------------------------------------------------------------------------------------|
| | Ketone pressure, mm | CH_4 pressure, mm | CO moles $\times 10^6$ | $\text{C}_3\text{F}_7\text{H}$ moles $\times 10^6$ | | |
| 439 | 24.0 | 43.4 | 5.20 | 0.606 | 3840 | 2.77 |
| 424 | 23.9 | 45.7 | 6.31 | 0.486 | 3780 | 1.83 |
| 382 | 21.7 | 42.0 | 5.52 | 0.124 | 3780 | 0.482 |
| 368 | 27.3 | 67.2 | 6.78 | 0.159 | 3420 | 0.356 |
| 343 | 20.2 | 49.3 | 6.48 | 0.052 ₃ | 4140 | 0.136 |
| 386 | 21.9 | 62.3 | 6.76 | 0.207 | 3840 | 0.497 |
| 400 | 26.7 | 66.1 | 8.04 | 0.340 | 4080 | 0.708 |
| 402 | 25.2 | 114.8 | 5.70 | 0.425 | 3780 | 0.643 |
| 355 | 26.8 | 96.5 | 8.56 | 0.121 | 3960 | 0.150 |
| 368 | 23.0 | 96.0 | 7.94 | 0.181 | 3960 | 0.244 |

The mechanism postulated for the reaction with methane is the following:





TABLE IV
THE REACTION OF $n\text{-C}_3\text{F}_7$ RADICAL WITH ETHANE

| Temp., °K | Reactants | | Products | | | | Time, sec | $\text{cc}^{\frac{1}{2}} \frac{k_2/k_2^{\frac{1}{2}}}{\times 10^{12}} \text{sec}^{-\frac{1}{2}}$ | $k_{3/a}/k_{3/b}$ |
|--------------|---------------------------|--------------------------------------------------|---------------------------------|--------------------------------------------------------------|---------------------------------------------------------------------------|-------------------------------------------------------------|--------------|--------------------------------------------------------------------------------------------------|-------------------|
| | Ketone pressure, mm | C ₂ H ₄ pressure, mm | CO moles ×10 ⁶ | C ₃ F ₇ H moles ×10 ⁶ | C ₃ F ₇ H ₃ moles ×10 ⁶ | C ₄ H ₁₀ moles ×10 ⁶ | | | |
| 379 | 22.1 | 20.6 | 7.24 | 1.99 | (>0.730) | Negligible | 3600 | 10.5 | |
| 423 | 22.1 | 8.9 | 8.16 | 2.76 | 1.49 | 0.031 | 3840 | 43.7 | 0.40 |
| 360 | 22.6 | 21.1 | 9.40 | 1.54 | 0.84 | 0.011 | 4200 | 6.17 | 0.40 |
| 402 | 26.4 | 22.1 | 12.2 | 5.38 | 2.99 | 0.06 | 4740 | 20.0 | 0.39 |
| 372 | 20.8 | 20.3 | 9.17 | 2.03 | 1.11 | 0.02 | 4140 | 8.52 | 0.41 |
| 400 | 17.3 | 19.6 | 6.98 | 2.95 | 1.58 | 0.047 | 3780 | 19.5 | 0.39 |
| 425.5 | 20.5 | 16.2 | 8.54 | 4.66 | 2.39 | 0.16 | 4200 | 37.2 | 0.40 |
| 433 | 19.4 | 20.1 | 4.96 | 4.06 | 2.31 | 0.24 | 4020 | 44.7 | 0.37 |
| 469 | 18.4 | 14.5 | 4.04 | 4.46 | 2.08 | 0.32 | 3720 | 135 | 0.40 |
| 455 | 18.9 | 16.5 | 5.30 | 4.12 | 1.87 | 0.30 | 4020 | 81.3 | 0.42 |

TABLE V
THE REACTION OF $n\text{-C}_3\text{F}_7$ RADICAL WITH DEUTERIUM-METHANE MIXTURES*

| Temp., °K | CH_4 pressure/ D_2 pressure | 51/52 ratio corrected | $k_3/k_{2'}$ |
|--------------|-----------------------------------------------|--------------------------|--------------|
| 370 | 1.52 | 3.38 | 2.22 |
| 421 | 1.56 | 1.95 | 1.25 |
| 396 | 1.92 | 2.87 | 1.50 |
| 358 | 1.49 | 3.71 | 2.49 |
| 397 | 1.38 | 2.00 | 1.45 |
| 382 | 1.22 | 2.26 | 1.85 |
| 455 | 1.36 | 1.23 | 0.905 |

*Total pressures were of the order of 50–60 mm Hg— $k_3/k_{2'}$ calculated from $R_{\text{C}_3\text{F}_7\text{H}}[\text{D}_2]/R_{\text{C}_3\text{F}_7\text{D}}[\text{CH}_4]$.

Fluorine abstraction reactions are ruled out by the absence of C_3F_8 in the products and no other reaction of importance in determining the amount of products seems to be possible. The rate of production of C_6F_{14} is thus very simply given by:

$$[1] \quad R_{\text{C}_6\text{F}_{14}} = R_{\text{CO}} - \frac{1}{2}(R_{\text{C}_3\text{F}_7\text{H}} + R_{\text{C}_4\text{H}_3\text{F}_7}).$$

The last column of Table III shows the values of

$$k_3/k_2^{\frac{1}{2}} = R_{\text{C}_3\text{F}_7\text{H}}/R_{\text{C}_6\text{F}_{14}}^{\frac{1}{2}} [\text{CH}_4]$$

calculated in this way,* and Fig. 1 shows the Arrhenius plot obtained. Least squares fitting of this plot give:

$$k_3/k_2^{\frac{1}{2}} = 1.25 \times 10^{-8} e^{-9.5 \times 10^3/RT} \text{ molecule}^{-\frac{1}{2}} \text{ cc}^{\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}. \text{ The value for } E_3 - \frac{1}{2}E_2 \text{ is thus } 9.5 \pm 0.5 \text{ kcal/mole.}$$

The mechanism for the ethane reaction is somewhat more complicated owing to the possibility of disproportionation in radical-radical reactions:



*Under the conditions of the experiments the quantities of $\text{C}_4\text{H}_3\text{F}_7$ were so small that no accurate analysis was possible. Their exclusion from [1] cannot affect the value of $k_3/k_2^{\frac{1}{2}}$ by more than one per cent. They have therefore been omitted from the table.

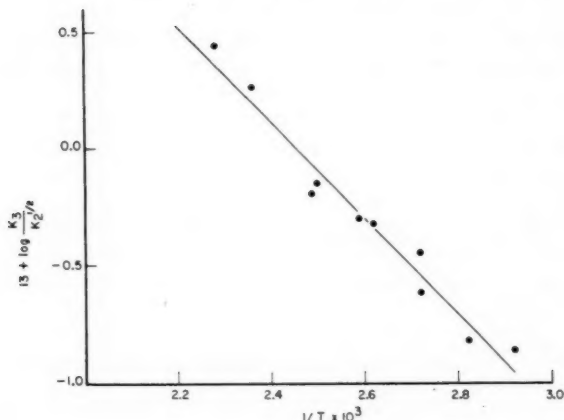


FIG. 1.

The stoichiometric balance can be carried out in this case by analyzing the products for CO, $\text{C}_3\text{F}_7\text{H}$, C_4H_{10} , and $\text{C}_5\text{F}_7\text{H}_5$ and assuming the ratio $k_{4'a}/k_{4'b}$ to be known. The best experimental value for the latter is 0.12, practically independent of temperature and pressure (4). The C_3F_7 radical balance will give the rate of formation of C_6F_{14} as in the former case:

$$R_{\text{C}_6\text{F}_{14}} = R_{\text{CO}} - \frac{1}{2}[R_{\text{C}_3\text{F}_7\text{H}} + R_{\text{C}_5\text{F}_7\text{H}_5}].$$

The balance for C_2H_5 radicals will give both the rate of formation of $\text{C}_3\text{F}_7\text{H}$ from reaction [3'] and the ratio $k_{5'a}/k_{5'b}$:

$$\begin{aligned} (R_{\text{C}_3\text{F}_7\text{H}})_{3'} &= \frac{1}{2}[R_{\text{C}_3\text{F}_7\text{H}} + R_{\text{C}_5\text{F}_7\text{H}_5} + 2.24 R_{\text{C}_4\text{H}_{10}}] \\ k_{5'a}/k_{5'b} &= [R_{\text{C}_3\text{F}_7\text{H}} - (R_{\text{C}_3\text{F}_7\text{H}})_{3'}]/R_{\text{C}_5\text{H}_5\text{F}_7} \end{aligned}$$

The justification of this procedure is indicated by the constancy of the value obtained for the latter expression over a range of temperatures as shown in Table IV. The table also gives the values of $k_{3'}/k_2^{1/2}$ obtained from

$$k_{3'}/k_2^{1/2} = (R_{\text{C}_3\text{F}_7\text{H}})_{3'}/R_{\text{C}_6\text{F}_{14}}^{1/2} [\text{C}_2\text{H}_6].$$

The Arrhenius plot of Fig. 2 gives for $E_{3'} - \frac{1}{2}E_2$ a value of 9.2 ± 0.5 kcal/mole and the expression for the rate is

$$k_{3'}/k_2^{1/2} = 2.24 \times 10^{-7} e^{-9.2 \times 10^3/RT} \text{ mole}^{-1/2} \text{ cc}^{1/2} \text{ sec}^{-1/2}.$$

The experiments in which methane and deuterium were put together into the reaction cell were devised to get a relative value of k_3 with respect to the rate constant of the reaction:



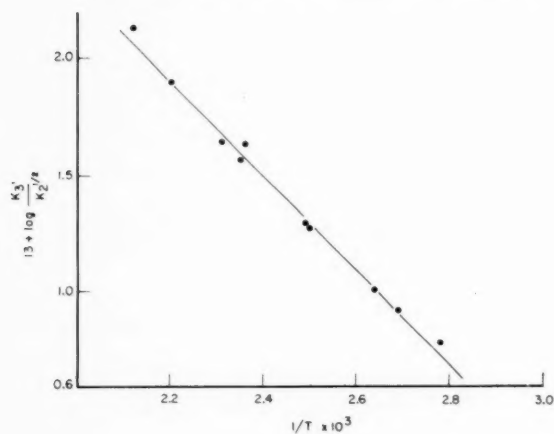


FIG. 2.

This method has already been used for the CF_3 radical by Pritchard and co-workers (5) and is simply based on the mass spectrographic estimation of the ratio RD/RH in the products. Some uncertainty arises from the fact that the fate of the D atoms produced in the abstraction is not known. In this case the possibilities are:



Table V gives the results of the runs performed at a total pressure of 60 to 70 mm of mercury. The Arrhenius plot is shown in Fig. 3 and the value for $E_3 - E_{3'}$ is found to be -3.4 ± 0.3 kcal/mole, the full expression for the ratio being:

$$k_3/k_{3'} = 1.99 \times 10^{-2} e^{3.42 \times 10^3/RT}$$

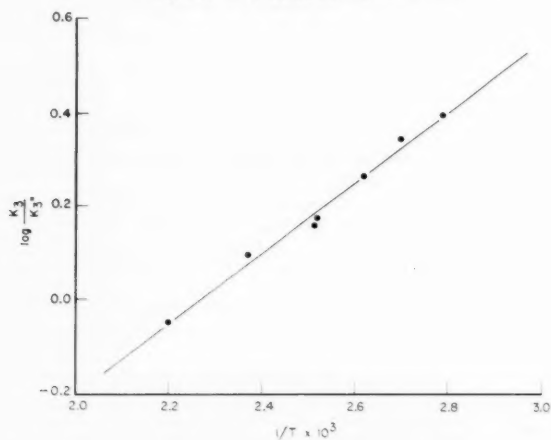


FIG. 3.

DISCUSSION

An absolute result for reaction [3''] is obtained from our data quite independently of the one obtained by Miller and Steacie (3). The value of $E_{3''}$, $-\frac{1}{2}E_2$ obtained in the present work is 12.9 ± 0.8 kcal/mole, which checks with the former value of 13.8 ± 0.5 , within experimental error. A comparison of the frequency factors is probably of little significance, given the somewhat large error in the activation energies. On the other hand, a comparison of the rate values in the temperature range of the experiments may be useful. At 400° K the value of Miller and Steacie (calculated assuming only reaction III to occur) is 0.24×10^{-13} molecule $^{-\frac{1}{2}}$ cc $^{\frac{1}{2}}$ sec $^{-\frac{1}{2}}$ and in the present case a reasonable agreement with that value is obtained also neglecting reaction III: 0.27×10^{-13} molecule $^{-\frac{1}{2}}$ cc $^{\frac{1}{2}}$ sec $^{-\frac{1}{2}}$. Although the uncertainty in these values is only within a factor of 2, which may be of little or no significance for these experiments, the almost complete agreement between our rate value and the former one seems to show that the same mechanism is operative in both cases. Possible occurrence of reaction IV in our case might also give a reason for the discrepancy of almost one kilocalorie per mole in our activation energy.

It is of interest to compare data for the methane, ethane, and hydrogen reactions with C_3F_7 and other radicals such as CH_3 and CF_3 for which sufficiently reliable data are available. In Table VI the activation energies, frequency factors, and the rate constants at 400° K are listed for these reactions.

TABLE VI
SUMMARY OF DATA ON REACTIONS: $R'H + R \rightarrow RH + R'^*$

| R = | CH ₃ | | | CF ₃ | | | C ₃ F ₇ | | |
|-------------------------------|----------------------|-----------------------------------|--------------------------------------|----------------------|-----------------------------------|--------------------------------------|-------------------------------|-----------------------------------|--------------------------------------|
| R'H | $E - \frac{1}{2}E_R$ | $A/A_R^{\frac{1}{2}} \times 10^8$ | $k/k_R^{\frac{1}{2}} \times 10^{13}$ | $E - \frac{1}{2}E_R$ | $A/A_R^{\frac{1}{2}} \times 10^8$ | $k/k_R^{\frac{1}{2}} \times 10^{13}$ | $E - \frac{1}{2}E_R$ | $A/A_R^{\frac{1}{2}} \times 10^8$ | $k/k_R^{\frac{1}{2}} \times 10^{13}$ |
| H ₂ | 10.0 ^a | 28.1 ^a | 3.0 | 8.8 ^a | 10.8 ^a | | 12.3 ^c | 56.3 ^c | |
| (D ₂) | 11.8 ^a | 16.7 ^a | | 9.7 ^a | 7.5 ^a | | 13.8 ^c | 77.6 ^c | |
| CH ₄ | 13.0 ^b | 3.3 | 0.029 ^b | 10.3 ^b | 12.5 | 3.5 ^b | 9.5 ^d | 1.25 ^d | 0.81 |
| C ₂ H ₆ | 10.4 ^b | 3.6 | 0.83 ^b | 7.5 ^b | 12.1 | 104 ^b | 9.2 ^d | 22.4 ^d | 20.4 |

*The subscript R refers to the recombination reaction $R + R \rightarrow R_2$. Units for k 's and A 's are molecules $^{-1}$ cc. sec $^{-1}$. E 's in kcal/mole.

^aFrom ref. 5.

^bFrom Steacie, E. W. R. J. Chem. Soc. 3991 (1956).

^cFrom ref. 3.

^dObtained in the present work.

It is very difficult to find some trend in the activation energies or in the frequency factors. The only general feature is that activation energies for the D₂ reactions are always 1.5 to 2.0 kcal/mole greater than those for H₂ and this seems to be due to the zero energy effect (3).

A striking feature can be noted in the behavior of the rate constants, however. It is apparent that great changes in reactivity (over 100-fold variation) are shown by the different radicals reacting with the hydrocarbons, while the hydrogen reaction is more or less insensitive to changes in the attacking radical.

It seems that there are two quite different types of reaction. It is interesting in this respect to point out that in the case of $R + H_2$ there is an almost linear relationship between $\log A$ and E for the three different radicals. Such a "compensation" behavior has been found already in other cases, and there has been a recent attempt to justify it on theoretical grounds (6), especially for the case of diatomic molecules. Such a relationship does not hold for $R + R'H$ where, on the other hand, a different regularity is

apparent. The relative reactivity of each radical toward methane and ethane is approximately constant, as shown by the ratio of the rate values of Table VI. This behavior is analogous to the findings of Smid and Szwarc for radical abstractions and additions in solution (7). It will be of interest to see if the mentioned regularities still hold in reactions with other similar radicals.

The value of the disproportionation-to-recombination ratio for the reaction between C_3F_7 and C_2H_6 is the first one reported for a reaction between a completely fluorinated radical and a completely hydrogenated one. Since C_3F_7 is seemingly more reactive toward hydrocarbons than CH_3 the ratio was expected to be greater than the one reported for $CH_3 + C_2H_6$, which is of the order of 0.03 (8); this expectation is amply justified by the value found, 0.40.

ACKNOWLEDGMENT

The authors wish to thank Miss B. Thornton for the mass spectrometric analyses.

REFERENCES

1. AYS COUGH, P. B. and STEACIE, E. W. R. *Proc. Roy. Soc. A*, **234**, 476 (1956).
2. MILLER, G. H., PRITCHARD, G. O., and STEACIE, E. W. R. *Z. physik. Chem.* **15**, 262 (1958).
3. MILLER, G. H. and STEACIE, E. W. R. *J. Am. Chem. Soc.* (In press).
4. KUTSCHKE, K. O., WIJNEN, M. H. J., and STEACIE, E. W. R. *J. Am. Chem. Soc.* **74**, 714 (1952).
5. PRITCHARD, G. O., PRITCHARD, H. O., and TROTMAN-DICKENSON, A. F. *Trans. Faraday Soc.* **52**, 849 (1956).
6. RÜETSCHI, P. *Z. physik. Chem.* **14**, 277 (1958).
7. SMID, J. and SZWARC, M. *J. Am. Chem. Soc.* **79**, 1534 (1957).
8. AUSLOOS, P. and STEACIE, E. W. R. *Can. J. Chem.* **33**, 1062 (1955).

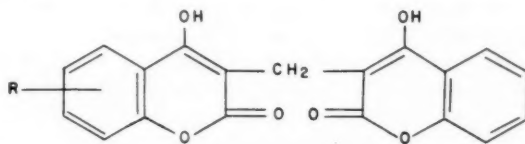
UNSYMMETRICALLY SUBSTITUTED 3,3'-METHYLENE BRIDGED 2,2'-DIHYDROXYCHROMONES^{1,2}

R. A. ABRAMOVITCH AND J. R. GEAR

ABSTRACT

Unsymmetrically substituted dicoumarol derivatives* have been synthesized by taking advantage of the fact that 4-hydroxycoumarins will undergo the Mannich reaction at C₃ and also take part in Michael-type addition reactions. In the presence of methyl iodide, 4-hydroxy-3-*N*-piperidinomethylcoumarin and 4-hydroxycoumarin gave dicoumarol. By using monosubstituted 4-hydroxycoumarins a variety of unsymmetrically substituted dicoumarols have been prepared in good yield. The infrared spectra of some of the intermediates and products are reported and discussed.

A large variety of substituted derivatives of the anticoagulant dicoumarol have been prepared with a view to the production of a more active product having less side effects. These compounds fall into two main groups: (i) those bearing a substituent on the bridge methylene group are generally prepared by condensing an aldehyde or ketone with 4-hydroxycoumarin; (ii) symmetrically disubstituted dicoumarols, prepared by condensing a substituted 4-hydroxycoumarin derivative with formaldehyde, as well as combinations of (i) and (ii). Neither of these methods is amenable to the preparation of unsymmetrically substituted derivatives (I) of dicoumarol, which are of a twofold interest: (a) as possible physiologically active analogues of dicoumarol; (b) a monohydroxylated dicoumarol may be an active metabolic product of the anticoagulant but this hypothesis has never been tested owing to the unavailability of such hydroxy-dicoumarols. We have now developed a method which appears to be fairly general for the synthesis of this type of compound.



The methylene group at C₃ in 4-hydroxycoumarin is reactive and will undergo Michael addition with suitably activated double bonds. For instance, addition will take place across the double bond in ethylidenacetone (1). Sullivan *et al.* (2) suggest that formation of dicoumarol itself from formaldehyde and 4-hydroxycoumarin proceeds by this type of addition: the unstable 3-methylene-2,4-diketochroman is first formed; this is very reactive and cannot be isolated but reacts quickly with another molecule of 4-hydroxycoumarin to form dicoumarol, this last step involving a Michael addition.

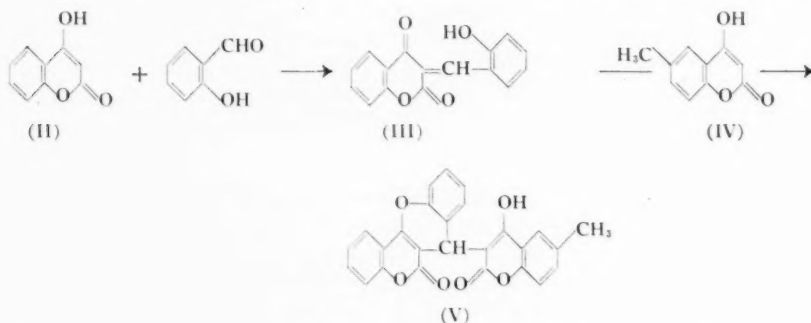
¹Manuscript received May 15, 1958.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

²This article is based on a paper presented at the 41st Annual Conference and Exhibition of the Chemical Institute of Canada, Toronto, May 26-28, 1958.

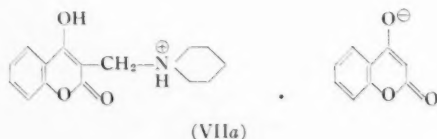
*The chemical name for dicoumarol is 3,3'-methylenebis(2-hydroxychromone) (see p. 1506). On this basis the name of ring-monosubstituted derivatives becomes very clumsy, e.g., 2-hydroxy-7-methyl-3-chromonyl-2-hydroxy-3-chromonylmethane. We propose to use the name dicoumarol to represent the ring system of 3,3'-methylenebis(2-hydroxychromone) and this practice will be adhered to throughout this paper.

They obtained support for this suggestion by condensing 4-hydroxycoumarin (II) with an equimolar quantity of salicylaldehyde to give 3-(*o*-hydroxybenzylidene)-2,4-diketochroman (III), which could be isolated, and which reacted with 4-hydroxy-6-methylcoumarin (IV) to give (V), indicating the stepwise nature of the reaction. Incidentally, (V) was the only example of a derivative of an unsymmetrically substituted



dicoumarol we were able to find in the literature. If 3-methylene-2,4-diketochroman could be generated *in situ* in the presence of a substituted 4-hydroxycoumarin derivative, addition would take place to give the required type of compound. Condensation of 4-hydroxycoumarin with formaldehyde, in the presence of a substituted 4-hydroxycoumarin was ruled out, since this would probably give rise to an inseparable mixture of dicoumarol derivatives. On the other hand, formation of the activated double bond *in situ* from a Mannich base was considered particularly suitable, since, by taking advantage of the active methylene at C₃, Robertson and Link (3) and also Prochazka (4) introduced a variety of aminomethyl groups in that position.

Heating together an equimolar mixture of 4-hydroxy-3-*N*-piperidinomethylcoumarin (VI) and 4-hydroxycoumarin (II) gave a highly insoluble 'addition complex' whose molecular composition corresponded to the sum of one mole of (VI) and one of (II). In view of the insolubility and instability of this complex its structure could be that of a salt of the type (VIIa).



It was hoped that the infrared spectrum would shed some light onto its structure, so that it was first necessary to study the spectrum of 4-hydroxycoumarin and that of 4-hydroxy-3-*N*-piperidinomethylcoumarin, and then to see what changes took place when these two combined to form the complex.

Infrared Spectra of 4-Hydroxycoumarins

4-Hydroxycoumarin can exist in a number of tautomeric modifications, but, according to Arndt (5), because of resonance stabilization the two main forms are the 4-hydroxycoumarin (II) and the 2-hydroxychromone (VIII) structures (see also ref. 5b).



As to which form predominates seems to depend on the experimental conditions and the nature of the substituents if present. From a study of the reactions of 4-hydroxycoumarin Kloss (6) concluded that the 4-hydroxycoumarin form (II) was favored but that under special conditions of solvent or acidity the chromone form could be favored. On the other hand, from a consideration of the ultraviolet spectra of 4-hydroxycoumarins in ethanol solution, Garden, Hayes, and Thomson (7) suggested that in this solvent 4-hydroxycoumarins could exist in the keto form (whether structures of types (VIII), or the diketonic structure, were meant is not clear).

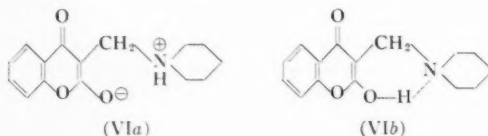
It should be possible to distinguish between structures (II) and (VIII) by infrared spectroscopy: (II) should exhibit a band for an α,β -unsaturated six-membered ring lactone at *ca.* 1710 cm^{-1} (8), whereas (VIII) should have a band at *ca.* 1660 cm^{-1} corresponding to the $\alpha,\beta,\alpha',\beta'$ -di-unsaturated ketone (9), and none at 1710 cm^{-1} . An elegant application of this principle is seen in the elucidation of the structures of novobiocin and its degradation products; novobiocin and 3-acetamido-7-acetoxy-4-hydroxy-8-methylcoumarin exist in the 4-hydroxycoumarin form ($\lambda_{\text{max}} 5.92\text{ }\mu$) (10), whereas if a free —OH group is present at $\text{C}_{(7)}$ as in dihydronovobiocic acid (10) or in 4,7-dihydroxycoumarin (more correctly called 2,7-dihydroxychromone) (11) the chromone structure is the stable form ($\lambda_{\text{max}} 6.0\text{ }\mu$). Similarly, the infrared spectra of 4-hydroxycoumarin, 4-methoxycoumarin, and 2-methoxychromone in the carbonyl region were studied by Knobloch and Prochazka (12). In dilute ethylene chloride solution 4-hydroxy- and 4-methoxycoumarin exhibited a single strong band at *ca.* 1710 cm^{-1} (with a medium intensity shoulder at 1700 cm^{-1}) corresponding to the α,β -unsaturated six-membered lactone structure, indicating that in that solvent 4-hydroxycoumarin probably exists exclusively in the 4-hydroxy form. On the other hand, 2-methoxychromone showed a single strong band at *ca.* 1650 cm^{-1} corresponding to the $\alpha,\beta,\alpha',\beta'$ -di-unsaturated ketonic stretching motion. Again, Wildi (13) reports a single band at $5.90\text{ }\mu$ for 4-hydroxy-3-phenylcoumarin in chloroform solution, together with a weak —OH stretching band at $2.87\text{ }\mu$.

Because of solubility and stability considerations it was only possible to measure the spectrum of the 'addition complex' obtained above as a Nujol mull so that it was desirable to study the spectrum of 4-hydroxycoumarin and 4-hydroxy-3-*N*-piperidinomethylcoumarin under such conditions. The spectrum of 4-hydroxycoumarin in the solid state is much more complex than the solution spectrum. There was no —OH band at *ca.* $2.9\text{ }\mu$ but a medium shoulder was present at 3125 cm^{-1} together with two medium peaks at 2730 and 2560 cm^{-1} , indicating that the —OH group is strongly bonded. In the carbonyl region two bands were present: at 1700 (s) (with an ill-defined shoulder at 1709) and at $1673\text{ cm}^{-1}\text{(s)}$, the latter being the stronger of the two. The spectrum of 4-hydroxy-7-methoxycoumarin is rather similar* with bands at 3125 (sh)(m) , 2760 (w) , 2620 (w) , 1707 (s) (medium shoulder at 1714 cm^{-1}), and $1672\text{ cm}^{-1}\text{ (ms)}$. It seems rather unlikely

*This spectrum is very similar to that obtained by Dr. R. H. Thomson and co-workers using the KBr disk technique. We understand that they have made an infrared study of 4-hydroxycoumarins, which is due to be published soon, but as our limited study was necessary for an interpretation of our results we are including it here. We would like to thank Dr. Thomson for sending us a tracing of the spectrum of 4-hydroxy-7-methoxycoumarin in KBr.

that the strong band at 1673 cm^{-1} should be due to the conjugated $\text{C}=\text{C}$ in the 4-hydroxy form; the band for this group is probably merged with the strong broad band at 1618 cm^{-1} . There are two possible interpretations for the presence of the two carbonyl stretching bands at 1700 and 1673 cm^{-1} . One is that in the solid state the compound is a mixture of the two tautomeric modifications, (II) giving rise to the higher and (VIII) to the lower band. Alternatively, the 1673 cm^{-1} band could arise from partial intermolecular hydrogen bonding between the $-\text{OH}$ group of one molecule and the lactone carbonyl group of another; the two bands would then be due to a mixture of chelated and unchelated lactone carbonyl groups in the solid state. In dilute ethylene chloride solution, such chelation would not take place and only the band at *ca.* 1710 cm^{-1} would be observed. This would also fit the fact that a chloroform solution of 4-hydroxy-3-phenylcoumarin has a single band at $5.90\text{ }\mu$ and a weak $-\text{OH}$ band at $2.87\text{ }\mu$ (13) (though in this case the steric effect of the phenyl substituent might prevent effective intermolecular chelation). If the first interpretation is accepted one would have to assume that in ethylene chloride solution the 4-hydroxycoumarin form is stabilized with respect to the chromone structure. On the basis of the present evidence it does not seem possible as yet to decide between the two alternatives. The same remarks apply also to 4-hydroxy-7-methoxycoumarin, which again exhibits no peak at 3450 cm^{-1} ; in this case the 1672 cm^{-1} peak is somewhat weaker than the 1701 cm^{-1} one and completely resolved from it.

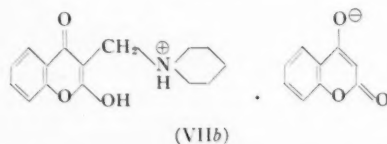
4-Hydroxy-3-N-piperidinomethylcoumarin has no hydroxyl band in the $3\text{ }\mu$ region (in Nujol mull). There are two bands at 2765 (m) and $2610\text{ cm}^{-1}\text{ (w)}$, but only a single band is present at 1678 cm^{-1} . The Mannich base, therefore, either exists in the chromone form in the solid state, or is completely intermolecularly chelated, which is less likely. The absence of an $-\text{OH}$ band could be due to such a chelation but could also be explained by internal salt formation (VIa) or internal hydrogen bonding (VIb).



In the absence of a band at $2440\text{--}2350\text{ cm}^{-1}$ for an R_3NH^+ grouping (14) (VIb) seems the more probable structure.

The spectrum of the 'addition complex' in Nujol mull shows bands at 3170 (m) (broad) (bonded $-\text{OH}$), 2750 (m) , 2730 (sh)(m) , 2570 (m) , 2470 (m) (R_3NH^+), 1719 (s) (α,β -unsaturated δ -lactone), and $1672\text{ cm}^{-1}\text{ (s)}$ ($\alpha,\beta,\alpha',\beta'$ -di-unsaturated $\text{C}=\text{O}$). These fit structure (VIIb) rather well.*

The chemical evidence was also in accord with this ammonium salt structure for the

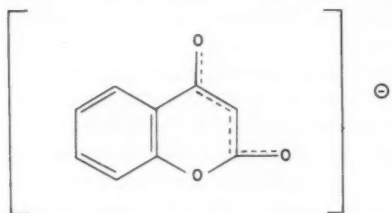


*For footnote see NOTE on p. 1505.

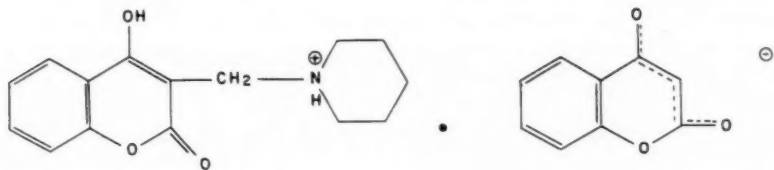
addition complex. Thus, it could not be recrystallized without decomposition; two recrystallizations from nitromethane transformed it completely into dicoumarol, which was also obtained by heating the complex with mineral acid. These properties are in accord with the known reactivity of Mannich bases quaternary salts (15). The structure postulated for the complex led us to the expectation that if 4-hydroxy-3-*N*-piperidinomethylcoumarin was quaternized with methyl iodide before treatment with 4-hydroxycoumarin (II), then the addition complex would not be formed and heating with (II) should lead to dicoumarol readily. This was fully confirmed by experiment, no complex being formed and dicoumarol (I, R = H) being obtained in good yield.

It was now necessary to prove that the reaction had taken place by the addition of the added 4-hydroxycoumarin to the 2,4-diketo-3-methylenechroman formed *in situ* from the Mannich base, and not by a partial reversal of the Mannich condensation followed by addition of the 4-hydroxycoumarin so formed to the chroman (the yield of dicoumarol obtained in the reaction already excludes this possibility). This was readily done by treating 4-hydroxy-3-*N*-piperidinomethylcoumarin methiodide with 4-hydroxy-7-methylcoumarin to give 7-methyldicoumarol (I; R = 7-CH₃-) which could also be obtained from 4-hydroxy-7-methyl-3-*N*-piperidinomethylcoumarin methiodide and 4-hydroxycoumarin. Because of possible ambiguity owing to the closeness of analytical figures

NOTE: Drs. K. P. Link and S. Preiss have kindly informed us that they have observed a broad band at 1635 cm⁻¹ in the spectrum of the sodium salt of 4-hydroxycoumarin, presumably corresponding to the anion



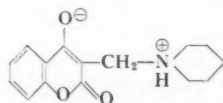
No band at 1719 cm⁻¹ was observed. They suggest, therefore, that structure (VIIc) would fit the infrared data also.



(VIIc)

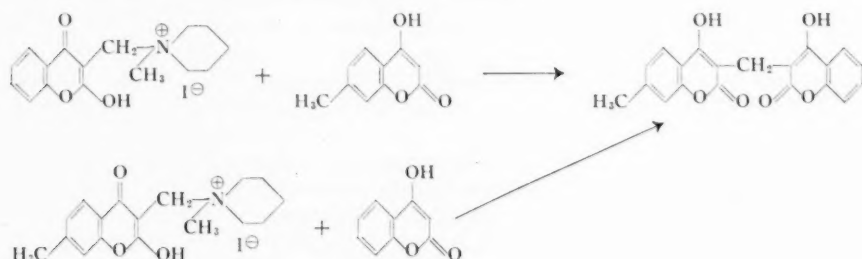
The fact that we observed a sharp band at 1672 cm⁻¹ for this compound at a much higher frequency than the broad band for the anion seems to speak against this possibility though it does not rule it out by any means. We would like to thank Drs. Link and Preiss for pointing the possibility out to us.

Structure



for the 3-piperidinomethyl derivative is ruled out by the absence of a band at 2440-2350 cm⁻¹.

7,7'-dimethyldicoumarol was also prepared for comparison and shown to be different from the unsymmetrical dicoumarol obtained above.



Having established the nature of the reaction, a number of unsymmetrically substituted dicoumarols were prepared to examine its scope; 6-methyl-, 6-chloro-, and 7-hydroxy-dicoumarol were readily obtained in good yields from 4-hydroxy-3-*N*-piperidinomethylcoumarin methiodide and the corresponding substituted 4-hydroxycoumarin. With 4-hydroxy-7-methoxycoumarin a product was readily obtained which consisted mainly of the expected 7-methoxydicoumarol, m.p. 245–248°, as shown by analysis, ultraviolet and infrared spectra, and by demethylation to the 7-hydroxydicoumarol prepared above. A small proportion of the product, however, was a highly insoluble higher melting (290–292°) substance for which good carbon and hydrogen analytical values could not be obtained. That it was a dicoumarol derivative was shown by its infrared spectrum (dicoumarols have a very characteristic type of absorption bands in the 6 μ region) which, apart from the fact that it had one extra band at 1110 cm^{-1} (m), was practically identical with that of 7-methoxydicoumarol. Also its ultraviolet absorption spectrum in dioxan solution was very similar to that of 7-methoxydicoumarol, differing only slightly in the ratios of the intensities of the peaks, indicating that the chromophoric systems were probably the same. The starting 4-hydroxy-7-methoxycoumarin was a pure compound, as shown by a comparison of its melting point and infrared spectrum with that of a specimen kindly supplied by Dr. R. H. Thomson, and also by demethylating it to the known 2,7-dihydroxychromone. The higher melting by-product was not investigated further at this stage. The infrared spectra of the dicoumarols were measured and are reported in the experimental section. They are in accord with the results of Knobloch and Prochazka (12) and will not be discussed here (dicoumarol has been represented by the 4,4'-dihydroxydicoumarin formula throughout this paper for convenience, though the infrared data indicate that the correct structure is that of a 2,2'-dihydroxydichromone with strongly intramolecularly chelated —OH groups (see ref. 12)).

The method described here for the synthesis of unsymmetrically substituted dicoumarols seems to be of general application. It is probable that it can be extended to dicoumarols bearing a substituent at the bridge methylene group by using aldehydes other than formaldehyde in the Mannich reaction.

EXPERIMENTAL

The melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 21 instrument using sodium chloride optics. Ultraviolet absorption spectra were measured with a Beckmann DK 2 recording spectrophotometer.

Reaction between 4-Hydroxycoumarin and 4-Hydroxy-3-N-piperidinomethylcoumarin

4-Hydroxy-3-N-piperidinomethylcoumarin was best prepared by the method of Robertson and Link (3).

(i) Without Methyl Iodide

Pure 4-hydroxycoumarin (0.164 g) and 4-hydroxy-3-N-piperidinomethylcoumarin (0.26 g) were dissolved in hot absolute ethanol (5 ml) and the solution boiled under reflux for 10 minutes. After 3 minutes a crystalline solid began to separate out. The cooled suspension was filtered, and the addition complex (A) (0.386 g) washed with a little hot alcohol. The product, m.p. 255–257°, could not be recrystallized without decomposition. It was insoluble in ethanol, benzene, chloroform, and carbon tetrachloride but soluble in dioxan, tetrahydrofuran, acetic acid, cyclohexanone, and dimethyl formamide. One recrystallization from nitromethane gave impure product, m.p. 258–260°, and a second recrystallization from the same solvent converted the material into dicoumarol, m.p. 293–295°, undepressed on admixture with an authentic specimen. For analysis purposes, (A) was washed repeatedly with hot alcohol and dried, the melting point remaining unchanged at 255–257°. Found: C, 68.35; H, 5.5. Calc. for $C_{24}H_{23}O_6N$: C, 68.3; H, 5.5%.

Heating the addition complex (0.386 g) in ethanol with concentrated hydrochloric acid (2 drops) for 1½ hours gave dicoumarol (0.129 g, 89.5%), m.p. 290–292°.

Infrared spectrum of the addition complex (Nujol mull) (main peaks only): 3170 (m) (broad), 2750 (m), 2730 (sh) (m), 2570 (m), 2470 (m), 1719 (s), 1672 (s), 1618 (s) (broad), 915 (m), 768 (s), 684 cm^{-1} (w).

(ii) Using Methyl Iodide

4-Hydroxy-3-N-piperidinomethylcoumarin (0.13 g) was dissolved in absolute ethanol (3 ml) and treated with an excess of methyl iodide (1 ml; if molar quantities are used only the addition complex (A) is obtained). 4-Hydroxycoumarin (0.082 g) in hot ethanol (3 ml) was added and the solution boiled under reflux for 4 hours, during which time dicoumarol gradually separated out. The product (0.151 g) was collected and recrystallized from cyclohexanone giving pure dicoumarol, m.p. 289–292°. Found: C, 68.21; H, 3.36. $C_{19}H_{12}O_6$ requires C, 68.0; H, 3.6%.

Infrared spectrum (Nujol mull) (main peaks only): 2770 (w), 2650 (w), 1663 (s), 1640 (s), 1612 (s), 1575 (s), 1555 (m), 1112 (s), 913 (m), 772 (s), 751 (m), 742 cm^{-1} (s).

4-Hydroxy-7-methyl-3-N-piperidinomethylcoumarin

A solution of piperidine (0.73 ml) and formaldehyde (0.5 ml, 38%) in absolute ethanol (5 ml) was added to a boiling solution of 4-hydroxy-7-methylcoumarin (1.0 g) in absolute ethanol (10 ml) and the mixture kept at 5° in the refrigerator for 3 days. The solid which separated (1.42 g), m.p. 177–179°, was recrystallized by dissolving it in hot ethanol and adding anhydrous ether until a turbidity appeared and then allowing to stand. After three such recrystallizations the pure base, m.p. 173–174°, was obtained. Found: C, 70.27; H, 7.04. Calc. for $C_{16}H_{19}O_3N$: C, 70.31; H, 7.01%.

*7-Methyldicoumarol**(i) From 4-Hydroxy-7-methylcoumarin*

A solution of 4-hydroxy-3-N-piperidinomethylcoumarin (0.259 g) in ethanol was treated with methyl iodide (1 ml) and after heating for a few minutes a solution of 4-hydroxy-7-methylcoumarin (0.174 g) in hot ethanol was added and the mixture boiled under reflux for 3 hours. The solid which separated (0.31 g), m.p. 256–259°, was recrystallized from cyclohexanone giving 7-methyldicoumarol, m.p. 261–262°. Found: C,

68.80; H, 3.97. Calc. for $C_{20}H_{14}O_6$: C, 68.5; H, 4.03%. Infrared spectrum (Nujol mull) (main peaks only): 2755 (w), 2620 (w), 1658 (s), 1633 (s), 1613 (s), 1570 (m), 1555 (sh)(m), 1105 (s), 805 (m), 777 (m), 755 (m), 738 cm^{-1} (m).

The product was different from both dicoumarol and 7,7'-dimethyldicoumarol.

In the absence of methyl iodide the corresponding addition complex, m.p. 234–236°, was obtained in 70% yield. It, too, decomposed to give the dicoumarol on attempted recrystallization, and a specimen pure enough for analysis could not be obtained.

(ii) *From 4-hydroxy-7-methyl-3-N-piperidinomethylcoumarin*

Methyl iodide (1 ml) was added to a solution of 4-hydroxy-7-methyl-3-N-piperidinomethylcoumarin (0.273 g) in absolute ethanol, the solution heated for 5 minutes, and 4-hydroxycoumarin (0.162 g) in hot ethanol added. After boiling under reflux for 5 minutes the product began to separate. The mixture was refluxed for another 2½ hours, cooled, filtered, and the solid (0.245 g), m.p. 255–258°, recrystallized from cyclohexanone to give 7-methyldicoumarol, m.p. 255–257°, undepressed on admixture with the specimen obtained as under (i).

7,7'-Dimethyldicoumarol

Formaldehyde (2 ml, 38%) was added to a boiling solution of 4-hydroxy-7-methyldicoumarol (0.5 g) in 50% ethanol (50 ml) and the solution boiled for 5 minutes giving impure product (0.484 g), m.p. 273–293°. Recrystallization from glacial acetic acid gave 7,7'-dimethyldicoumarol, m.p. 292–294°, depressed to 260–270° on admixture with 7-methyldicoumarol. Found: C, 69.24; H, 4.47. Calc. for $C_{21}H_{16}O_6$: C, 69.2; H, 4.44%. Anschutz (16) gives m.p. 273–275° for this compound.

6-Methyldicoumarol

This was obtained in 89.4% yield from 4-hydroxy-6-methylcoumarin, 4-hydroxy-3-N-piperidinomethylcoumarin, and methyl iodide. It had m.p. 250–251° (from cyclohexanone). Found: C, 68.57; H, 4.01. Calc. for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03%.

6-Chlorodicoumarol

This was similarly obtained from 6-chloro-4-hydroxycoumarin, 4-hydroxy-3-N-piperidinomethylcoumarin, and methyl iodide. Yield 90.3%. Recrystallization from cyclohexanone gave pure product, m.p. 266–268°. Found: C, 62.2; H, 2.93. Calc. for $C_{19}H_{11}O_6Cl$: C, 61.6; H, 3.00%. Infrared spectrum (Nujol mull) (main peaks only): 2720 (w), 2595 (w), 1657 (s), 1632 (s), 1607 (m), 1576 (m), 1500 (w), 1109 (m), 914 (w), 809 (w), 765 cm^{-1} (m).

7-Methoxydicoumarol

4-Hydroxy-7-methoxycoumarin was prepared from 2-hydroxy-4-methoxyacetophenone, diethyl carbonate, and pulverized sodium by the method of Desai and Sethna (17) and was identical in melting point (mixed melting point undepressed) and infrared spectrum with a specimen kindly supplied by Dr. R. H. Thomson (Aberdeen University, Scotland).

4-Hydroxy-3-N-piperidinomethylcoumarin (5.2 g) in absolute ethanol (50 ml) was treated with a large excess of methyl iodide (20 ml). 4-Hydroxy-7-methoxycoumarin (3.84 g) in ethanol (80 ml) was then added and the mixture boiled under reflux for 4 hours. The cooled suspension was filtered and the solid, m.p. 245–260°, extracted three times with boiling glacial acetic acid. On cooling, the combined extracts deposited slightly impure 7-methoxydicoumarol (5.0 g), which on recrystallization from glacial acetic acid gave product (4.9 g), m.p. 245–248°. Further recrystallizations from acetic acid did not raise the melting point. Found: C, 65.41; H, 4.05. Calc. for $C_{20}H_{14}O_7$: C, 65.57;

H, 3.85%. Infrared spectrum (Nujol mull) (main peaks): 1655 (s) (broad), 1620 (s), 1602 (s), 1565 (s), 1512 (m), 1098 (s), 835 (m), 805 (m), 775 (m), 752 (m), 740 cm^{-1} (sh)(m). Ultraviolet spectrum (in dioxan solution): λ_{max} 323 (infl.), 317, 307 (infl.), 289 $\text{m}\mu$ $10^{-3} \epsilon$: 35.99, 29.95, 37.52, 29.95.

The residue (0.5 g) from the acetic acid extraction was recrystallized from cyclohexanone giving colorless crystals, m.p. 290–292°. Good analytical figures could not be obtained for this compound (found: C, 64.17; H, 4.45%), which differed greatly in solubility from the 7-methoxydicoumarol, m.p. 245–248°, obtained above. The infrared spectrum was identical with that of 7-methoxydicoumarol except for a single weak peak at 1110 cm^{-1} which was absent in the spectrum of the lower melting product. The ultraviolet spectrum measured in dioxan is very similar to that of 7-methoxydicoumarol indicating that no change has occurred in the chromophoric system. λ_{max} 324 (infl.), 317, 307 (infl.), 289 $\text{m}\mu$ $10^{-3} \epsilon$ (assuming the same molecular weight as 7-methoxydicoumarol): 35.44, 40.12, 33.70, 20.33.

4,7-Dihydroxycoumarin (2,7-Dihydroxychromone)

A mixture of 4-hydroxy-7-methoxycoumarin (0.8 g) and anhydrous aluminum chloride (4 g) in dry benzene (150 ml) was boiled under reflux for 6 hours. Crushed ice and dilute hydrochloric acid were then added to the cold mixture and the benzene evaporated off giving 4,7-dihydroxycoumarin (0.74 g), m.p. 265–268°, which could be recrystallized from dilute methanol. Bauer and Schoder (18) give m.p. 264° (decomp.) for this compound.

7-Hydroxydicoumarol

(i) 4-Hydroxy-3-*N*-piperidinomethylcoumarin (0.114 g) in absolute ethanol was treated with methyl iodide (2 ml) and then with 4,7-dihydroxycoumarin (0.75 g) and the mixture refluxed for 8 hours. Working up in the usual way gave 7-hydroxydicoumarol (0.115 g), m.p. 300–302°, which on recrystallization from glacial acetic acid had m.p. 300–302°. Found: C, 64.67; H, 3.79. Calc. for $\text{C}_{18}\text{H}_{12}\text{O}_7$: C, 64.77; H, 3.43%. Infrared spectrum (Nujol mull) (main peaks only): 3380 (m) (broad), 2740 (w), 2600 (w), 1655 (sh) (s), 1635 (s), 1608 (s), 1573 (s), 1315 (s), 1113 (s) (broad), 856 (m), 808 (m), 798 (m), 770 (s), 755 (s), 744 cm^{-1} (m).

(ii) 7-Methoxydicoumarol (0.5 g, m.p. 245–248°) and anhydrous aluminum chloride (2.5 g) in dry benzene (100 ml) were boiled under reflux for 8 hours. Cracked ice and dilute hydrochloric acid were added to the cold mixture, the benzene was removed, and the product recrystallized from glacial acetic acid giving 7-hydroxydicoumarol (0.321 g), m.p. 300–302° undepressed in admixture with material obtained as under (i) above. The infrared spectra of the two products were also identical.

ACKNOWLEDGMENTS

This work was carried out during the tenure (by J.R.G.) of a Thorvaldson Scholarship. We wish to thank Dr. R. H. Thomson (Aberdeen) for a specimen of 4-hydroxy-7-methoxycoumarin and Dr. L. Vining for the use of a Beckmann DK 2 recording spectrophotometer.

REFERENCES

1. IKAWA, M., STAHMANN, M. A., and LINK, K. P. J. Am. Chem. Soc. **66**, 902 (1944).
2. SULLIVAN, W. R., HUEBNER, C. F., STAHMANN, M. A., and LINK, K. P. J. Am. Chem. Soc. **65**, 2288 (1943).
3. ROBERTSON, D. N. and LINK, K. P. J. Am. Chem. Soc. **75**, 1883 (1953).
4. PRCHAZKA, Z. Chem. listy, **47**, 59 (1953).

- 5a. ARNDT, F., LOEWE, L., ÜN, R., and AYCA, E. Chem. Ber. **84**, 319 (1951).
- b. ARNDT, F. Problems in theoretical organic chemistry. 28th Annual Prestly Lectures. Phi Lambda Upsilon, University of Pennsylvania. 1954. p. 37.
6. KLOSA, J. Arch. Pharm. **286**, 37 (1953).
7. GARDEN, J. F., HAYES, N. F., and THOMSON, R. H. J. Chem. Soc. 3315 (1956).
8. JONES, R. N. and HERLING, F. J. Org. Chem. **19**, 1252 (1954).
9. THOMPSON, H. W. and TORKINGTON, P. J. Chem. Soc. 640 (1945).
10. STAMMER, C. H., WALTON, E., WILSON, A. N., WALKER, R. W., TRENNER, N. R., HOLLY, F. W., and FOLKERS, K. J. Am. Chem. Soc. **80**, 137 (1958).
11. SPENCER, C. F., RODIN, J. O., WALTON, E., HOLLY, F. W., and FOLKERS, K. J. Am. Chem. Soc. **80**, 140 (1958).
12. KNOBLOCH, E. and PROCHAZKA, Z. Chem. listy, **47**, 1285 (1953).
13. WILDI, B. S. J. Org. Chem. **16**, 407 (1951).
14. WITKOP, B. J. Am. Chem. Soc. **76**, 5597 (1954).
15. ADAMS, R. Organic reactions. Vol. 1. John Wiley & Sons, Inc., New York. 1942. p. 307.
16. ANSCHUTZ, R. Ann. **367**, 244 (1909).
17. DESAI, N. J. and SETHNA, S. J. Org. Chem. **22**, 388 (1957).
18. BAUER, K. G. and SCHODER, F. Arch. Pharm. **259**, 53 (1921).

RECIPROCAL SALT PAIRS, INVOLVING THE CATIONS Li_2 , Na_2 , AND K_2 , THE ANIONS SO_4 AND Cl_2 , AND WATER, AT 25°C ¹

A. N. CAMPBELL, E. M. KARTZMARK, AND E. G. LOVERING²

ABSTRACT

In the reciprocal salt pair Li_2 , K_2 , Cl_2 , SO_4 , and water, at 25°C there are large areas in which potassium sulphate and potassium lithium sulphate (KLiSO_4) are separately in equilibrium with solution. Two incongruent invariant points exist. At one of these the composition of the solution is 0.917 mole fraction chloride,³ 0.437 mole fraction lithium, and 19.4 moles of water per total mole of salt, the equilibrium solid phases being potassium chloride, potassium sulphate, and the double salt. At the second, the composition of the solution is 0.967 mole fraction chloride, 0.870 mole fraction lithium, and 13.8 moles of water per mole of salt, the solid phases being potassium chloride, double salt, and lithium sulphate monohydrate. One congruent invariant point exists, at which the composition of the solution is 1.00 mole fraction chloride, 0.960 mole fraction lithium, and 9.6 moles of water per mole of salt, the solid phases being lithium sulphate monohydrate, lithium chloride monohydrate, and potassium chloride.

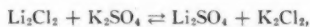
In the reciprocal salt pair Li_2 , Na_2 , Cl_2 , SO_4 , and water, at 25°C there is an incongruent invariant point at which the composition of the solution is 0.873 mole fraction chloride, 0.668 mole fraction lithium, and 15.1 moles water per total mole of salt, the solid phases being sodium chloride, solid solution of sodium and lithium sulphates, and lithium sulphate monohydrate. A congruent invariant point exists, at which the composition of the solution is practically entirely lithium chloride, the solid phases present being lithium chloride monohydrate, lithium sulphate monohydrate, and sodium chloride.

INTRODUCTION

The two reciprocal salt pairs



and



both at 25°C , which form the subject of this paper, are part of the five-component system: Li_2 , Na_2 , K_2 , Cl_2 , SO_4 , water, at 25°C , which is being studied in this department. The component ternary systems are now all known, as well as the two four-component systems: Li_2 , Na_2 , K_2 , Cl_2 , H_2O and Li_2 , Na_2 , K_2 , SO_4 , H_2O . The reciprocal salt pair:



is also known. Nothing has been done on the remaining two reciprocal salt pairs. A bibliography is appended to this paper (1a-1i, 2).

Particular mention should be made, however, of a recent paper by Cavalca and Nardelli (3), who claim that the double salt $\text{Na}_3\text{Li}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ exists at 27°C . This is not in agreement with the work of Campbell and Kartzmark (4), who found no double salt but extensive solid solution at 25°C . As a final check on this point, two experiments were carried out. Appropriate mixtures of lithium sulphate, sodium sulphate, and water were stirred for 1 week in contact with excess of solid at 25°C . The solutions and wet residues were analyzed, both by determination of sulphate as barium sulphate and by viscosity. When these results were plotted on the triangular diagram of Campbell and Kartzmark, the tie lines found by the unsatisfactory barium sulphate method crossed, while those found by the viscosity method did not. This may constitute an explanation of the results of Cavalca and Nardelli.

¹Manuscript received May 30, 1958.

²Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.

³Cominco Fellow, University of Manitoba, 1957-58.

⁴Throughout this paper mole fractions are calculated with double atomic weight for univalent ions, i.e., Li_2 , Na_2 , K_2 , and Cl_2 .

EXPERIMENTAL

All chemicals used were of the highest purity and they were not further purified by us but the sulphates were dried by fusion. Solutions and solid phases were analyzed by evaporating to dryness, igniting, and weighing. Chloride radical was determined gravimetrically as silver chloride. The remaining solid was converted to sulphate by treatment with sulphuric acid, followed by ignition. A fixed weight (10 or 20 g) of sulphate mixture was dissolved in water, made up to fixed volume (100 ml), and the viscosity determined. The value of the viscosity gave the ratio of the two cations present. Sulphate radical was determined by difference, since the gravimetric determination of sulphate, in the presence of alkali metals, is notoriously unsatisfactory, although we have occasionally been forced to use the method. The method described above works very well. It is necessary to heat the sulphated solids at 600° C, for not less than six hours, to ensure that no trace of free sulphuric acid has been left. The dried sulphate mixture was tested for the presence of free acid and chloride radical, before it was used further. Viscosity curves for the systems potassium sulphate-lithium sulphate and sodium sulphate-lithium sulphate were obtained for mixtures of known composition.

The nature of the solid phases present was revealed to some extent by the chemical analysis taken in conjunction with a knowledge of the general trend of the solubility curve under investigation, but recourse was made to other methods whenever possible. Thus, sodium sulphate decahydrate was identified by removing a few of the characteristic crystals and warming them slightly when they underwent the transition to anhydrous salt. Solid solution (in sodium salt) was suspected when the lithium content began to rise above that which might reasonably be attributed to adhering mother liquor. Lithium sulphate monohydrate was identified by its prismatic habit and the fact that it does not dehydrate on a steam bath. We found it impossible to use the polarizing microscope because it was necessary to dry the solid phase and this could change the nature of the solid phases. Similarly, X-ray diffraction photography was found to be useless here. The wet solid phases gave indefinite pictures. In the course of the X-ray work, however, it was found that the X-ray powder diffraction data for lithium sulphate monohydrate, as given in the file of the American Society for Testing Materials, were not complete. Powder pictures of this material were therefore taken and will be offered for publication elsewhere by one of us (E.G.L.).

The Jänecke method of graphical representation (5) was used. In this system of representation, ternary invariant points appear as points on the sides; water is expressed by isohydrates or lines of equal water content. Experimentally, we started from each invariant point on the sides of the diagram in turn, making sure that a plentiful excess of the two solid phases was present, and progressively added small quantities of a cation or anion which did not participate in the original equilibrium. Equilibrium was attained by stirring for 24 hours after each addition when liquid and solid phases were analyzed. Invariance in quaternary systems showed itself by the composition of the liquid phase becoming constant with further additions; it was then a question of identifying the third solid phase which had appeared. If a new ion appeared (in appreciable quantity) for the first time in the solid phase, there was seldom any doubt as to the nature of the new solid phase. Moreover, since no solid phase occurs in the quaternary systems other than those occurring in the component ternary systems, it was usually obvious when two solubility curves intersected what the new phase would be.

EXPERIMENTAL RESULTS

TABLE I

VISCOSITIES AND DENSITIES OF LITHIUM SULPHATE - POTASSIUM SULPHATE -
WATER SOLUTIONS AT 25° C
(10 g salt/100 ml)

| Wt. K ₂ SO ₄ (g) | Wt. Li ₂ SO ₄ (g) | Density (g/ml) | Viscosity (η H ₂ O = 1.0000) |
|-------------------------------------------|--------------------------------------------|-------------------|-----------------------------------------------------|
| 10 | 0 | 1.0738 | 1.1342 |
| 9 | 1 | 1.0741 | 1.1751 |
| 8 | 2 | 1.0748 | 1.2174 |
| 7 | 3 | 1.0752 | 1.2594 |
| 6 | 4 | 1.0758 | 1.3048 |
| 5 | 5 | 1.0757 | 1.3460 |
| 3 | 7 | 1.0770 | 1.4482 |
| 2 | 8 | 1.0776 | 1.4999 |
| 1 | 9 | 1.0780 | 1.5559 |
| 0 | 10 | 1.0780 | 1.6141 |

TABLE II

VISCOSITIES AND DENSITIES OF SODIUM SULPHATE - LITHIUM SULPHATE -
WATER SOLUTIONS AT 25° C
(20 g salt/100 ml)

| Wt. Na ₂ SO ₄ (g) | Wt. Li ₂ SO ₄ (g) | Density (g/ml) | Viscosity (η H ₂ O = 1.0000) |
|--------------------------------------------|--------------------------------------------|-------------------|-----------------------------------------------------|
| 20 | 0 | 1.1606 | 1.9057 |
| 18 | 2 | 1.1604 | 1.9699 |
| 16 | 4 | 1.1591 | 2.0369 |
| 14 | 6 | 1.1583 | 2.1071 |
| 12 | 8 | 1.1573 | 2.1817 |
| 10 | 10 | 1.1565 | 2.2552 |
| 8 | 12 | 1.1554 | 2.3356 |
| 6 | 14 | 1.1551 | 2.4231 |
| 4 | 16 | 1.1545 | 2.5163 |
| 2 | 18 | 1.1532 | 2.6125 |
| 0 | 20 | 1.1524 | 2.7016 |

DISCUSSION OF RESULTS

1. THE SYSTEM $K_2Cl_2 + Li_2SO_4 \rightleftharpoons K_2SO_4 + Li_2Cl_2$, AT 25° C

The equilibrium diagram is shown as Fig. 1. The curves representing two solid phases in equilibrium with solution are shown as heavy lines, the lighter lines being isohydres (lines of equal water content, expressed as moles of water per mole of total salts). The phase boundaries are usually drawn as straight lines because the experimental accuracy does not usually warrant indicating curvature. The isohydres are very approximate, owing to lack of data, but they do indicate the course of isothermal evaporation. The stable pair of solid phases, that is, the pair of salts that can exist in contact with each other and with solution, consists of lithium sulphate monohydrate and potassium chloride. There are three invariant points. At the invariant point 8, in Fig. 1, the solid phases are potassium sulphate, potassium chloride, and double salt (KLiSO₄). Since the invariant point does not fall within the composition triangle, whose angular points represent the three solid phases, it is incongruent. The invariant point 17, where lithium sulphate

monohydrate, potassium chloride, and double salt are in equilibrium with solution, is also incongruent. Point 21, where the solid phases are lithium chloride monohydrate, lithium sulphate monohydrate, and potassium chloride, is congruent.

TABLE III

THE COMPOSITION OF THE SOLUTIONS AND THE NATURE OF THE SOLID PHASES IN THE SYSTEM $\text{Li}_2\text{K}_2\text{Cl}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ AT 25°C

| Point No. | Composition of the liquid phase | | Moles of H_2O per mole of salt | Nature of the solid phases |
|-----------|---------------------------------|-----------------------------|------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|
| | Mole fraction Cl_2 | Mole fraction Li_2 | | |
| 1 | 0.959 | 0.140 | 21.9 | $\text{K}_2\text{Cl}_2 + \text{K}_2\text{SO}_4$ |
| 2 | 0.927 | 0.408 | 19.6 | $\text{K}_2\text{Cl}_2 + \text{K}_2\text{SO}_4$ |
| 3 | 0.167 | 0.594 | 29.2 | $\text{K}_2\text{SO}_4 + \text{LiKSO}_4$ |
| 4 | 0.582 | 0.557 | 27.5 | $\text{K}_2\text{SO}_4 + \text{LiKSO}_4$ |
| 5 | 0.700 | 0.543 | 26.3 | $\text{K}_2\text{SO}_4 + \text{LiKSO}_4$ |
| 6 | 0.822 | 0.487 | 23.6 | $\text{K}_2\text{SO}_4 + \text{LiKSO}_4$ |
| 7 | 0.467 | 0.880 | 21.0 | $\text{K}_2\text{SO}_4 + \text{LiKSO}_4$ |
| 8 | 0.916 | 0.437 | 19.4 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{K}_2\text{SO}_4$ |
| 9 | 0.917 | 0.435 | 19.4 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{K}_2\text{SO}_4$ |
| 10 | 0.918 | 0.439 | 19.4 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{K}_2\text{SO}_4$ |
| 11 | 0.933 | 0.562 | 18.5 | $\text{LiKSO}_4 + \text{K}_2\text{Cl}_2$ |
| 12 | 0.956 | 0.698 | 17.1 | $\text{LiKSO}_4 + \text{K}_2\text{Cl}_2$ |
| 13 | 0.157 | 0.952 | 17.7 | $\text{LiKSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 14 | 0.480 | 0.946 | 19.2 | $\text{LiKSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 15 | 0.740 | 0.933 | 19.0 | $\text{LiKSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 16 | 0.902 | 0.914 | 17.2 | $\text{LiKSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 17 | 0.967 | 0.874 | 13.8 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 18 | 0.967 | 0.870 | 13.8 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 19 | 0.966 | 0.870 | 13.8 | $\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 20 | 0.985 | 0.913 | 12.3 | $\text{K}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 21 | 1.000 | 0.960 | 9.6 | $\text{Li}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O} + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{K}_2\text{Cl}_2$ |

TABLE IV

THE COMPOSITION OF THE SOLUTIONS AND THE NATURE OF THE SOLID PHASES IN THE SYSTEM $\text{Li}_2\text{Na}_2\text{Cl}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ AT 25°C

| Point No. | Composition of the liquid phase | | Moles of H_2O per mole of salt | Nature of the solid phases |
|-----------|---------------------------------|-----------------------------|------------------------------------------------|----------------------------------------------------------------------------------------------------|
| | Mole fraction Cl_2 | Mole fraction Li_2 | | |
| 1 | 0.074 | 0.263 | 18.1 | $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ |
| 2 | 0.149 | 0.212 | 18.0 | $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ |
| 3 | 0.296 | 0.110 | 17.9 | $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ |
| 4 | 0.777 | 0.112 | 15.7 | $\text{Na}_2\text{Cl}_2 + \text{solid solution}$ |
| 5 | 0.822 | 0.451 | 15.6 | $\text{Na}_2\text{Cl}_2 + \text{solid solution}$ |
| 6 | 0.846 | 0.592 | 15.4 | $\text{Na}_2\text{Cl}_2 + \text{solid solution}$ |
| 7 | 0.872 | 0.669 | 15.1 | $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 8 | 0.871 | 0.679 | 15.1 | $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 9 | 0.880 | 0.660 | 15.2 | $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 10 | 0.918 | 0.733 | 15.3 | $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 11 | 0.890 | 0.695 | — | $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ |
| 12 | 0.758 | 0.681 | 16.2 | $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 13 | 0.701 | 0.683 | 16.4 | $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 14 | 0.489 | 0.692 | 16.2 | $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |
| 15 | 0.240 | 0.700 | 13.5 | $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{solid solution}$ |

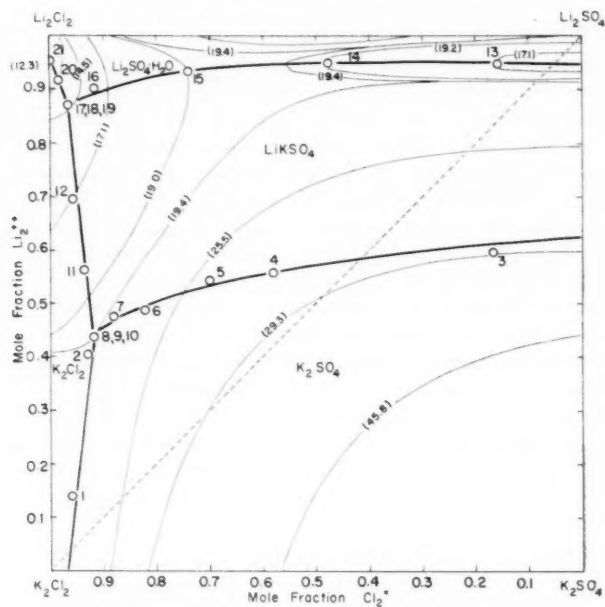


FIG. 1. The system lithium, potassium, chloride, sulphate, water, at 25° C.

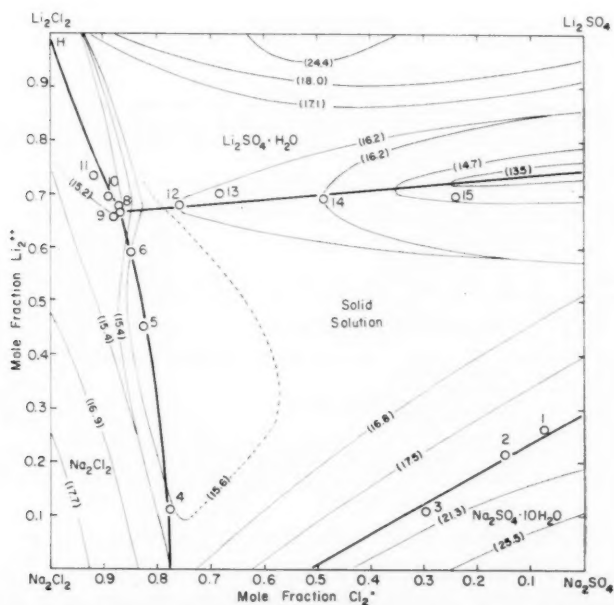


FIG. 2. The system lithium, sodium, chloride, sulphate, water, at 25° C.

2. THE SYSTEM $\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{Li}_2\text{Cl}_2$, AT 25°C

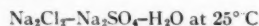
The equilibrium diagram is shown in Fig. 2. The stable salt pair is similar to the previous system, i.e., the coexistent salts are sodium chloride and lithium sulphate monohydrate. Since no double salt occurs in this system, there are only two invariant points, one congruent and the other not. At the incongruent invariant point (point 7), the solid phases in equilibrium with solution are lithium sulphate monohydrate, sodium chloride, and a solid solution of sodium and lithium sulphates; the amount of lithium in the solid solution increases as the concentration of lithium in the liquid phase increases. At point H, the congruent invariant point, the solid phases are lithium chloride monohydrate, lithium sulphate monohydrate, and sodium chloride; the solution is very rich in lithium chloride. It has been shown by Campbell and Kartzmark (4) that the double salt NaLiSO_4 exists above 29.3°C . It is conceivable that this double salt could exist, at 25°C , in contact with the solution containing lithium and sodium chlorides. If it did exist, three invariant points would appear, in place of point 7, at which the solid phases would be double salt and (1) $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{NaCl}$; (2) $\text{NaCl} + \text{solid solution}$; (3) $\text{solid solution} + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. All attempts to find such invariant points failed. It is known from the ternary system, $\text{Li}_2\text{Cl}_2\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ that the $\text{LiCl} \cdot \text{H}_2\text{O}$ field in the quaternary diagram must be extremely narrow; it cannot be investigated experimentally or expressed graphically to scale.

ACKNOWLEDGMENTS

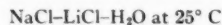
We are indebted to Dr. R. B. Ferguson, of the Department of Geology, for advice and assistance with the X-ray photography and to the Consolidated Mining and Smelting Company of Canada for financial assistance in the form of a Cominco Fellowship.

REFERENCES

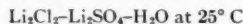
For the following ternary systems:



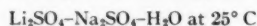
- 1a. MEYERHOFFER, W. and SAUNDERS, A. P. *Z. physik. Chem.* **28**, 453 (1899). SEIDELL, A. *Am. Chem. J.* **27**, 52 (1902). SCHREINEMAKERS, F. A. H. *Proc. Roy. Soc. Amsterdam*, **13**, 1163 (1911). BLASDALE, W. C. *Ind. Eng. Chem.* **10**, 344 (1918). TAKEGAMI, S. *Mem. Coll. Sci., Kyoto Imp. Univ.* **4**, 317 (1921).



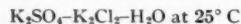
- 1b. SMITS, A., ELGERSMA, J., and HARDENBURG, E. M. *Rec. trav. chim.* **43**, 671 (1924).



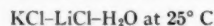
- 1c. SCHREINEMAKERS, F. A. H. and KAYSER, G. M. A. *Chem. Weekblad*, **15**, 120 (1918) (at 30°). DRUZHININ, I. G. and YANKO, A. P. *Doklady Akad. Nauk S.S.S.R.* **94**, 481 (1954).



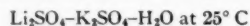
- 1d. CAVALCA, L. and NARDELLI, M. *Gazz. chim. ital.* **82**, 394 (1952). CAMPBELL, A. N. and KARTZMARK, E. M. *Can. J. Chem.* **36**, 171 (1958).



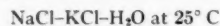
- 1e. MEYERHOFFER, W. and SAUNDERS, A. P. *Z. physik. Chem.* **28**, 453 (1899). BLASDALE, W. C. *Ind. Eng. Chem.* **10**, 344 (1918). ANOSOV, YA. V. and BYZOVA, E. A. *Izvest. Sectora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R.* **15**, 118 (1947).



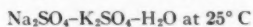
- 1f. CAMPBELL, A. N. and KARTZMARK, E. M. *Can. J. Chem.* **34**, 672 (1956).



- 1g. YANKO, A. P. and DRUZHININ, I. G. *J. Gen. Chem. U.S.S.R. (Eng. Transl.)*, **25**, 13 (1955). CAMPBELL, A. N. and KARTZMARK, E. M. *Can. J. Chem.* **36**, 171 (1958).

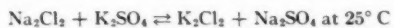


1*h*. BLASDALE, W. C. J. Ind. Eng. Chem. **10**, 344 (1918).



1*i*. HAMID, M. A. J. Chem. Soc. 201 (1926).

For the reciprocal salt pair:



2. MEYERHOFFER, W. and SAUNDERS, A. P. Z. physik. Chem. **28**, 453 (1899). BLASDALE, W. C. J. Ind. Eng. Chem. **10**, 344 (1918). D'ANS, J. A. Kali, **9**, 148, 161, 177, 193, 217, 219 (1915).
3. CAVALCA, L. and NARDELLI, M. Gazz chim. ital. **82**, 394 (1952).
4. CAMPBELL, A. N. and KARTZMARK, E. M. Can. J. Chem. **36**, 171 (1958).
5. JÄNECKE, E. Z. anorg. Chem. **51**, 132 (1906); **71**, 1 (1911).

THE KINETICS OF RADICAL REACTIONS IN THE TRACKS OF FAST ELECTRONS

A DETAILED STUDY OF THE SAMUEL-MAGEE MODEL FOR THE RADIATION CHEMISTRY OF WATER¹

P. J. DYNE AND J. M. KENNEDY

ABSTRACT

The kinetic behavior of a γ -ray spur produced in water, having H and OH radicals distributed spatially in the manner suggested by Samuel and Magee, has been studied using an electronic computer. The variation in yield of the molecular products H_2 , H_2O_2 , and H_2O with rate constants, diffusion constants, and spur size has been obtained. The model gives agreement with experiment choosing spurs with a small "radius" of the order of 10 Å. On simple assumptions, however, the model predicts no difference in the molecular yields between heavy and light water and no isotopic separation in the formation of molecular hydrogen from isotopically enriched light water. Various special assumptions needed to give agreement with experiment for these isotope effects are discussed. The observed isotopic separation in the formation of molecular hydrogen is attributed to the preferential dissociation of an H atom from an excited HDO molecule. It is found that the yield of molecular hydrogen is less sensitive to the presence of scavengers than the yield of hydrogen peroxide.

1. INTRODUCTION

The products of the radiation decomposition of water are of two types, free radicals and molecules, and it is generally supposed that the molecular products (hydrogen and hydrogen peroxide) are formed by recombination of free radicals (H and OH) in regions of high radical concentration. In the model of this process proposed by Samuel and Magee (1) it was suggested that the radicals were formed by the dissociation of excited water molecules. Consequently, both species of radicals have initially a similar spatial distribution; some of these radicals recombine to give molecular products, others escape by diffusion into the bulk of the solution where they can be detected by their reactions as radicals. Several variations of this model are discussed by Dewhurst, Samuel, and Magee (2).

While this model has been widely accepted for the interpretation of the radiation chemistry of water no detailed study of its properties has been made in which the recombination of both reacting species (H and OH) is treated. As the kinetics of recombination and diffusion cannot be handled analytically the majority of calculations hitherto have been performed on a simplified version, a "one radical" model in which the one species has the "average" properties of H and OH. These calculations have shown that the model explains many of the features of the radiation decomposition of water and on this pragmatic basis the model has been accepted.

We have surmounted the main obstacle to the study of a two-radical model, the intractable nature of the equations, by programming the problem for numerical solution on the Chalk River Datatron Computer, and this paper presents the results of these calculations. A second, equally serious, obstacle remains and this is our lack of knowledge about the rate constants and diffusion constants and other parameters of the system. We have, accordingly, adopted an approach which is essentially the converse of that of experimental chemical kinetics; the "constants" (rate constants, etc.) of the systems are treated as parameters. We derive graphical relations between these parameters and

¹Manuscript received July 14, 1958.

Contribution from the Research Chemistry and Theoretical Physics Branches, Atomic Energy of Canada Limited, Chalk River, Ontario.

Issued as A.E.C.L. No. 693.

the yields of radicals and molecular products. Our conclusions comprise a qualitative picture of the kinetic properties of the model, an estimate of the range of values of the parameters which will give agreement with experiment, and a discussion of the details of the isotope effects and scavenger effects.

2. THE SAMUEL-MAGEE MODEL

In their original paper Samuel and Magee (1) suggested that the passage of a high energy (1 Mev) β -particle through liquid water initiated the following sequence of events: the β -particle ionizes water molecules at widely spaced intervals along its track, each ionization forming a "spur". The ionized electron has, on the average, an energy of about 60 ev, which is rapidly lost as it ionizes and excites some of the surrounding water molecules forming, say, three H_2O^+ ions and three electrons. The ions recapture the ionized electrons after the electrons have been thermalized by collision with surrounding molecules and form excited water molecules. These in turn dissociate to give H atoms and OH radicals. The whole process from the initial ionization to the dissociation occurs in a time of the order of 10^{-13} seconds. The radicals are distributed inside a volume which is only a few molecular diameters across. For the purposes of calculation it was assumed that the initial distribution is given by a Gaussian with a modulus of 10 Å.

Samuel and Magee solved the kinetic equations for reaction and diffusion in a spur for the case of one species of radical where the spatial distribution was assumed *always* to be a Gaussian. This technique, known as the "Prescribed Diffusion Approximation", enabled them to calculate analytically the ratio of free radicals recombining to the total formed initially. They showed that for a "reasonable" choice of parameters, the calculated value agreed with experiment. These calculations were extended to the case of α -ray decomposition and tritium β -ray decomposition. With α -rays the primary ionizations lie very close together and the initial distribution consists of a column of radicals which expands in cylindrical symmetry; with tritium β -rays the spurs overlap quite shortly after their formation and recombination occurs partly in spherical and partly in cylindrical symmetry. Agreement with experiment for both these was obtained with the choice of parameters used for the calculation on high energy β -rays.*

3. THE TRACK EQUATION FOR THE TWO-RADICAL MODEL

The calculations on the "two-radical" model described in this paper deal only with the case of high energy β -rays, i.e. spurs which expand wholly in spherical symmetry with no overlapping. From these calculations we can predict differences in the behavior of H and OH and estimate the extent of recombination to reform H_2O which is not observable experimentally and which is not distinguished in a one-radical calculation from recombination to give H_2 and H_2O_2 .

We adopt the convention that the hydrogen atom is species 1 with diffusion constant D_1 and recombination rate constant k_{11} and concentration C_1 which is a function of time and space. The OH radical is species 2 with constants D_2 , k_2 , C_2 , etc. The rate constant for the recombination of H and OH radicals is k_{12} .

The track equations governing the kinetics reaction and diffusion are:

$$\partial C_1 / \partial t = D_1 \nabla^2 C_1 - [(N_1 - 1) / N_1] k_{11} C_1^2 - k_{12} C_1 C_2 - k_{1s} C_1 C_s, \quad [1]$$

$$\partial C_2 / \partial t = D_2 \nabla^2 C_2 - [(N_2 - 1) / N_2] k_{22} C_2^2 - k_{12} C_1 C_2 - k_{2s} C_2 C_s, \quad [2]$$

*Note added in proof: The results of some detailed computations on a one-radical model have recently been published by Flanders and Fricke, *J. Chem. Phys.* **28**, 1126 (1958).

where N_1 and N_2 are the total number of radicals in the spur at time t , k_{1s} and k_{2s} are the rate constants for reaction with scavenger present in a small, uniform concentration C_s . The yields of hydrogen, hydrogen peroxide in one spur, are the values of

$$\int_0^\infty \int_0^\infty k_{11} C_1^2 dv dt, \int_0^\infty \int_0^\infty k_{22} C_2^2 dv dt, \text{ and } \int_0^\infty \int_0^\infty k_{12} C_1 C_2 dv dt,$$

gives the amount of H_2O reformed in the spur. The quantities $(N_1-1)/N_1$ and $(N_2-1)/N_2$ are statistical factors which take into account the fact that, with a small number of radicals, the expression $k_{11}C_1^2$ must be reduced so that the bimolecular reaction of a radical with itself is not included, e.g. if there are six radicals in the spur, one particular radical can only react with five others and the rate is therefore 5/6 of the rate given by the standard kinetic expression.

The numerical method used is described in the Appendix.

4. THE INITIAL CHOICE OF CONSTANTS

Because none of the constants in the problem has been measured directly we have to estimate their order of magnitude a priori. As our object is to determine the sensitivity of the yields to variations in the constants, our initial choice is equivalent to defining the area to be explored. This is, of necessity, somewhat arbitrary.

First let $D_2 = 2 \times 10^{-5}$ cm²/second (the same as the self-diffusion constant for water) (3). It seems entirely reasonable that OH and H_2O will diffuse at comparable rates. As the hydrogen atom is lighter, D_1 must necessarily be greater than D_2 . Simple kinetic theory shows that the ratio $D_1/D_2 = \sqrt{(M_2/M_1)}$ where M_2 and M_1 are the masses of the two species. This gives $D_1 = 8 \times 10^{-5}$ cm²/second. The use of this formula is equivalent to assuming identical scattering cross sections for the diffusion of H and OH in water. This study is confined to cases where $D_1/D_2 \approx 4$.

The initial choice of the rate constants has been made with the aid of the Smoluchowski relation

$$k_{12} = A(\sigma_1 + \sigma_2)(D_1 + D_2), \quad [3]$$

where σ_1 and σ_2 are the collision diameters of the species 1 and 2. The value of A is discussed by Fricke (4) and following his arguments we have chosen a value of A so that k_{11} and k_{22} are both $\sim 1 \times 10^{-11}$ and 1×10^{-11} cc/molecule second. With $\sigma_1 = 0.5$ Å and $\sigma_2 = 1.5$ Å we chose $k_{11} = 1.2 \times 10^{-11}$, $k_{12} = 3.0 \times 10^{-11}$, and $k_{22} = 0.9 \times 10^{-11}$. The larger value of k_{12} is mainly due to the statistical factor of two, which distinguishes between the collision numbers for like particles and unlike particles.

The constants k_{1s} and k_{2s} were taken as 1×10^{-11} and C_s were taken as 10^{-3} M. Two further constants which do not appear explicitly in the track equation must also be fixed. These are the initial size of spur and the number of radicals per spur. Following Samuel and Magee the initial concentration is taken to be a Gaussian.

$$C_1(r) = (N_1^0 \beta^3 / \pi^{3/2}) \exp(-\beta^2 r^2) \quad [4]$$

where $1/\beta$ is the radius at which $C_1(r)$ has fallen to $1/e$ of its maximum value. No further assumption is made about the spatial distributions during the course of the reaction. We have taken $1/\beta = 10^{-7}$ cm = 10 Å which we denote by the symbol R . This value can be justified by noting that the spur is formed by the thermalization of a slow (50–70 eV) electron which excites, say, three to six water molecules during its lifetime. If the ex-

citation cross section is of the order of the gas kinetic cross section, the mean distance between excitations in liquid water is found to be $\sim 10 \text{ \AA}$. It follows that the value of 10 \AA for the modulus of a Gaussian distribution is reasonable.

No experimental evidence on the size and structure of spurs is available for water. The most relevant measurements are statistics of the number of ion pairs in spurs generated in the gas phase obtained by Wilson (5) and Beekman (6) from cloud chamber photographs. The former finds an "average" spur size of between two and three ion pairs. This is not the most probable size; according to Wilson, 40% of the spurs contains only one ion pair. Beekman finds 60% containing one ion pair. These measurements were made in air. Taking the energy per ion pair to be 32 volts, these data suggest an average energy deposition of 65 ± 10 volts/spur. The only direct measurement of the number of water molecules dissociated initially is obtained from Firestone's (7) studies of the radiation decomposition of water vapor where the medium is so dilute that no recombination occurs. He finds $G(-\text{H}_2\text{O}) = 11 \pm 1$. Combining this value with the value of 65 ± 10 volts per spur obtained above we obtain a value of 6 ± 1 radical pairs per spur and we have taken $N = 6$ in our calculations. Monchick, Samuel, and Magee (8) chose $N = 5$ but they did not discuss the reasons for their choice.

In this argument we assume that the "average" spur, in terms of average energy, is the "average" spur for the value of yields, etc., which we are interested in calculating. It is conceivable that the yields vary very sharply as a function of N so that the two averages are different. However, using some of the values of the yields calculated as a function of N and weighting these according to a distribution in N given by the above arguments we find that the "average" spur does correspond to a six-radical pair spur.

5. THE CALCULATIONS

The detailed results of the calculations are presented in Table I. The numbers to the left of the double line are the constants which specify the individual case; those to the right are the values of the yields in one spur. The yields of H_2 and H_2O_2 are expressed as the number of atoms or radicals which have recombined to give these products. The number of molecules formed is half this number. $[\text{H}_2\text{O}^*]$ is the number of water molecules reformed, $[-\text{H}_2\text{O}]$ is the net decomposition. If the number of hydrogen atoms in the spur is N_1 , we have

$$N_1 = N_2 = [\text{H}_2] + [\text{H}_2\text{O}^*] + [\text{H}] = [\text{H}_2\text{O}_2] + [\text{H}_2\text{O}^*] + [\text{OH}] = [\text{H}_2\text{O}^*] + [-\text{H}_2\text{O}], \quad [5]$$

using square brackets to symbolize the yields defined above.

From the computation of each case a plot like Fig. 1 is constructed which shows the course of the reaction as a function of time. Several features of the process are shown in this figure. A significant fraction of the total amount of recombination occurs in times of the order of 10^{-11} seconds but the process is not complete until some 10^{-8} seconds have elapsed. The scavenging reaction is, at concentrations of $\sim 10^{-3}$ molar, negligible until nearly 10^{-8} seconds have elapsed. The true yields of molecular products are given by the asymptotes to the curves in Fig. 1. These can be estimated, with sufficient accuracy, by a visual extrapolation at times of $\sim 10^{-8}$ seconds.

6. EXPERIMENTAL VALUES OF THE RADICAL AND MOLECULAR YIELDS

These calculations related to the decomposition of pure water; experimental G -values for this system are given in Table II. We are indebted to A. O. Allen and H. A. Schwarz

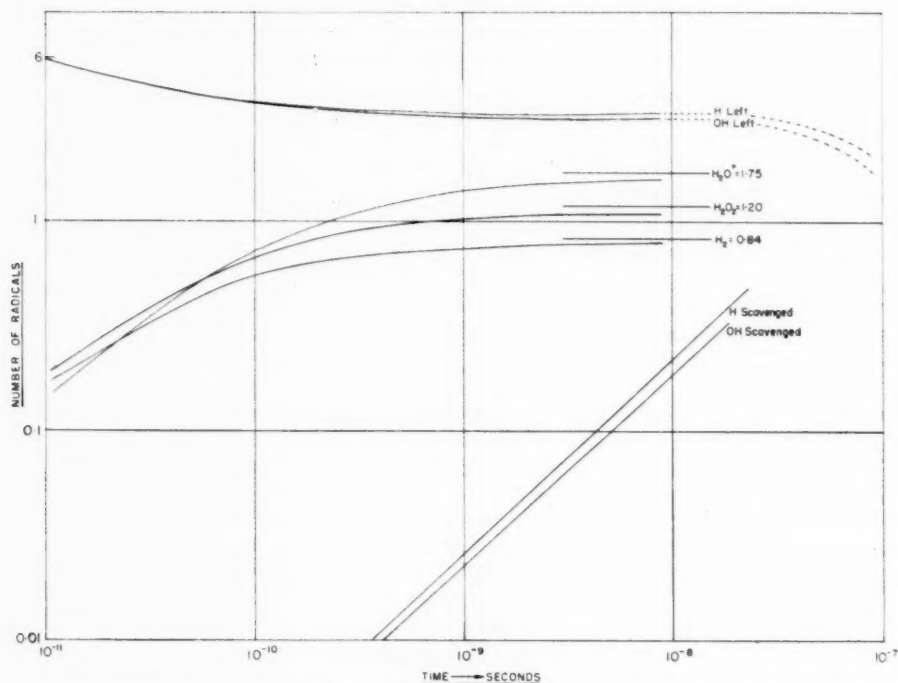


FIG. 1. Kinetics of recombination in a γ -ray spur for case I. The number of radicals which have recombined are plotted as a function of time together with the number which have not reacted. In times of the order of 10^{-7} – 10^{-6} seconds the number of unreacted radicals falls sharply as they are scavenged.

(private communication) for these numbers which in their opinion represent "the best values for γ -rays acting in neutral water containing vanishingly small amounts of active solutes" which suppress the reaction of H with H_2O_2 and of OH with H_2 . The second line expresses these numbers as the number of atoms or radicals of one species which have combined to give the observed yield. This is the form used in Table I.

This table contains two different kinds of information. Firstly, adopting the Samuel-Magee interpretation, it follows that of the hydrogen atoms involved in the *net* decomposition (see equation [5]) a fraction, which we shall call $f(\text{H}_2)$, recombine to give molecular hydrogen. From Table II we see that $f(\text{H}_2) = 0.90/3.7 = 0.23$ and that the analogous quantity for OH radicals $f(\text{H}_2\text{O}_2) = 1.40/3.7 = 0.38$. The second kind of information is the value of the yields per unit of energy absorbed and this is summarized by saying that $G(-\text{H}_2\text{O}) = 3.7$.

7. YIELDS AS A FUNCTION OF THE OVER-ALL VALUES OF RATE CONSTANTS AND DIFFUSION CONSTANTS

One would expect the amount of recombination to depend critically on the *ratio* of the values of the rate constants to the values of the diffusion constants. It is obvious from an inspection of the track equation that if this ratio is fixed then the yield is determined; the absolute value of the constants determines the *time* in which the recombination

TABLE I
 COMPUTED MOLECULAR AND RADICAL YIELDS FOR γ -RAY SPURS

The columns to the left of the double line refer to the parameters of the spur and are explained in sections 3 and 4. The columns to the right of the double line give the computed yields which are defined in section 6.

| | k_{11} $\times 10^{11}$ | k_{12} $\times 10^{11}$ | k_{22} $\times 10^{11}$ | D_1 $\times 10^6$ | D_2 $\times 10^6$ | $N_1 = N_2$ | $\beta_1 = \beta_2$ $\times 10^{-2}$ | $k_8 C_8$ | | | | | | |
|--------------------------------------|------------------------------|------------------------------|------------------------------|------------------------|------------------------|-------------|-----------------------------------------|-------------------|-------------------|----------------------------------|---------------------|------|------|---------------------|
| | | | | | | | | | | | | | | |
| | | | | | | | | | [H ₂] | [H ₂ O ₂] | [H ₂ O*] | [H] | [OH] | [-H ₂ O] |
| A Initial case | 1.2 | 3.0 | 0.9 | 8.0 | 2.0 | 6.0 | 1.0 | 6.0×10^6 | 0.56 | 1.10 | 2.50 | 2.94 | 2.40 | 3.50 |
| B Changing all k 's and D 's | 0.4 | 1.0 | 0.3 | 2.1 | 1 | 2 | 1 | 1 | 0.19 | 0.33 | 0.75 | 0.88 | 0.72 | 1.00 |
| C Changing all k 's | " | " | " | 8.0 | 2.0 | " | " | " | 0.32 | 0.76 | 1.45 | 4.23 | 3.79 | 4.55 |
| D " " " " | " | " | " | " | " | " | " | " | 0.80 | 1.15 | 3.60 | 1.60 | 1.25 | 2.40 |
| E Changing both D 's | 1.2 | 3.0 | 0.9 | 3.0 | 0.75 | " | " | " | 0.78 | 1.15 | 3.50 | 1.72 | 1.35 | 2.50 |
| F " " " " | 3.6 | 9.0 | 2.7 | " | " | " | " | " | 0.42 | 0.94 | 1.85 | 3.73 | 3.21 | 4.15 |
| G Varying k_{11} | 3.6 | " | " | 15.0 | 3.75 | " | " | " | 1.40 | 1.20 | 2.25 | 2.35 | 2.55 | 3.75 |
| H " " " " | 10.0 | " | " | 8.0 | 2.0 | " | " | " | 2.35 | 1.35 | 1.90 | 1.75 | 2.75 | 4.10 |
| I Varying k_{12} | 1.2 | 1.0 | " | " | " | " | " | " | 0.84 | 1.20 | 1.75 | 3.41 | 3.05 | 4.25 |
| J " " " " | 1.2 | 9.0 | " | " | " | " | " | " | 0.30 | 0.49 | 4.00 | 1.70 | 1.51 | 2.00 |
| K Varying k_{22} | 1.2 | 3.0 | 2.7 | " | " | " | " | " | 0.60 | 2.10 | 2.30 | 3.10 | 1.60 | 3.70 |
| L " " " " | " | " | 8.1 | " | " | " | " | " | 0.67 | 3.0 | 1.8 | 3.53 | 1.2 | 4.2 |
| M Isotope effect | 0.8484 | 2.296 | 0.90 | 5.657 | " | " | " | " | 0.56 | 1.10 | 2.50 | 2.94 | 2.40 | 3.50 |
| N Vary k_{11} and D_1 | 0.6 | 3.0 | 0.9 | 4.0 | " | " | " | " | 0.42 | 0.85 | 3.25 | 2.33 | 1.90 | 2.75 |
| O Varying scavenger concentration | 1.2 | 3.0 | 0.9 | 8.0 | 2.0 | 6.0 | 1.0 | 6.0×10^6 | 0.56 | 1.10 | 2.50 | 2.04 | 2.30 | 3.50 |
| P " " " " | " | " | " | " | " | " | " | 6×10^7 | 0.55 | 1.05 | 2.40 | 3.15 | 2.55 | 3.60 |
| Q " " " " | " | " | " | " | " | " | " | 6×10^8 | 0.49 | 0.79 | 2.10 | 3.31 | 3.11 | 3.80 |
| R " " " " | " | " | " | " | " | " | " | 6×10^9 | 0.33 | 0.39 | 1.32 | 4.35 | 4.29 | 4.38 |
| S Varying spur size | " | " | " | " | " | " | 2.0 | 6×10^6 | 0.76 | 1.25 | 3.40 | 1.84 | 1.35 | 2.60 |
| T " " " " | " | " | " | " | " | " | " | 6×10^6 | 0.41 | 0.86 | 1.80 | 3.79 | 3.34 | 4.20 |
| U Varying no. of radicals per spur | " | " | " | " | " | 2.0 | 1.0 | " | 0.056 | 0.13 | 0.49 | 1.45 | 1.38 | 1.51 |
| V " " " " | " | " | " | " | " | 3.0 | " | " | 0.15 | 0.34 | 0.95 | 1.90 | 1.71 | 2.05 |
| W " " " " | " | " | " | " | " | 9.0 | " | " | 1.10 | 1.90 | 4.40 | 3.50 | 2.70 | 4.60 |
| X " " " " | " | " | " | " | " | 15.0 | " | " | 2.40 | 3.60 | 8.50 | 4.10 | 2.90 | 6.50 |
| Y Vary size of spur for H atoms only | " | " | " | " | " | " | $\beta_1 = 0.65$ $\beta_2 = 1.0$ | " | 0.41 | 1.40 | 2.10 | 3.49 | 2.50 | 3.90 |
| Z " " " " | " | " | " | " | " | " | $\beta_1 = 0.4$ $\beta_2 = 1.0$ | " | 0.28 | 1.70 | 1.41 | 4.31 | 2.89 | 4.59 |

 TABLE II
 G-VALUES (YIELDS/100 EV) IN PURE WATER

| | $G(\text{H}_2)$ | $G(\text{H}_2\text{O}_2)$ | $G(\text{H})$ | $G(\text{OH})$ | $G(-\text{H}_2\text{O})$ |
|-----|-----------------|---------------------------|---------------|----------------|--------------------------|
| (a) | 0.45 | 0.70 | 2.8 | 2.3 | 3.7 |
| (b) | 0.90 | 1.40 | 2.8 | 2.3 | 3.7 |

(a) Yields expressed conventionally.

(b) Yields expressed as number of atoms or radicals which have combined to give these species.

occurs. This is demonstrated numerically by comparing case (A) with case (B). For brevity we shall refer to cases simply by letter, e.g. (A), (B), just as we are symbolizing the yields per spur by the use of square brackets, e.g. [H₂], [-H₂O]. In (B) all the k 's and all the D 's have been divided by three but the yields are unchanged.

The variation of yields as the ratio of all the k 's to the D 's is changed is shown by (A), (C), and (D). In these cases the ratios $k_{11}:k_{12}:k_{22}$ are unchanged as are the values of D_1 and D_2 . The yields, plotted as a function of k_{12} , are shown in Fig. 2: values of $f(\text{H}_2)$ and $f(\text{H}_2\text{O}_2)$ are plotted in Fig. 3. The values of [H₂] and [H₂O₂] are not very sensitive to the simultaneous variation of the constants as these recombination processes are working in competition with the recombination to form H₂O. The values of $f(\text{H}_2)$ and $f(\text{H}_2\text{O}_2)$ are however very sensitive to changes in the values of the rate constants.

An inspection of Fig. 3 shows that agreement with experimental values is obtained in a

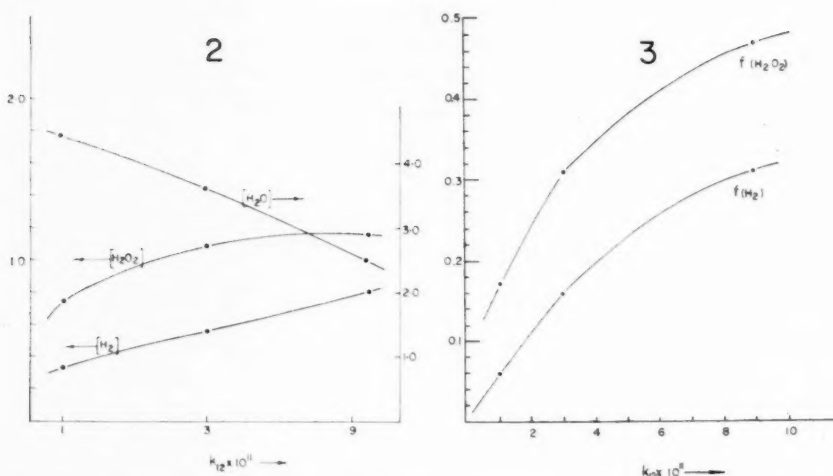


FIG. 2. Variation of yields with the over-all value of constants k_{11} , k_{12} , k_{22} plotted as a function k_{12} . Cases (A), (C), and (D). k_{12} is plotted on a logarithmic scale.

FIG. 3. Variation of $f(H_2)$ and $f(H_2O_2)$ with over-all value of constants k_{11} , k_{12} , k_{22} plotted as a function of k_{12} . Cases (A), (C), and (D).

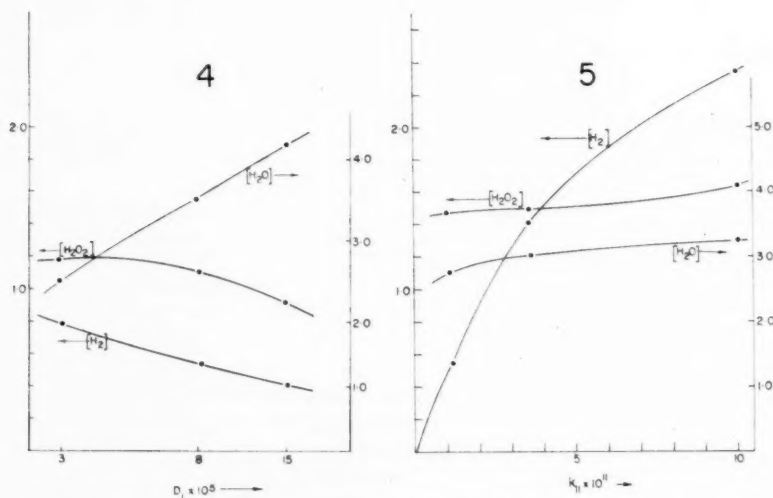


FIG. 4. Variation of yields with the over-all value of the diffusion constants, plotted against D_1 . Cases (A), (E), and (F). D_1 is plotted on a logarithmic scale.

FIG. 5. Variation in yields with the value of k_{11} . Cases (A), (G), and (H).

fairly sharply defined region. The values of $f(H_2)$ and $f(H_2O_2)$ depend on the ratios $k_{11} : k_{12} : k_{22}$ and we can only make the qualitative statement that the k 's must be of the order of $2-6 \times 10^{-11}$ cc/molecule second to obtain agreement with experiment.

This simple point is worth re-emphasizing; for a spur of the size postulated the a

priori choice of diffusion constants and rate constants gives a strikingly sharp region of experimental agreement. The yields are, of course, a function of the initial size of the spur as discussed in Section 10.

Similar arguments apply to the over-all variation of the diffusion constants exemplified by (E), (A), and (F), whose yields are plotted in Fig. 4 as a function of D_1 . This figure is a mirror image of Fig. 2—again exemplifying the fact that the yield depends only on the ratio of the rate constants to the diffusion constants.

Experimentally $G(\text{H}_2\text{O}_2)$ is about 80% greater than $G(\text{H}_2)$ and it is apparent from Table I that most of the cases give figures in this ratio. A similar comparison can be made for $G(\text{H})$ and $G(\text{OH})$. These inequalities are explained in this model by the large difference in diffusion constant between H and OH which outweighs the small difference between k_{11} and k_{22} which acts in the opposite direction ($k_{11} > k_{22}$).

8. YIELDS AS A FUNCTION OF THE INDIVIDUAL VALUES OF THE RATE CONSTANTS

Yields as a function of k_{11} are covered by (G) and (H) and plotted in Fig. 5, as a function of k_{12} are covered by (I) and (J) and plotted in Fig. 6, and as a function of k_{22} are covered by (K) and (L) and plotted in Fig. 7.

The curves show the expected form. $[\text{H}_2]$ is strongly dependent on k_{11} but not on k_{22} and $[\text{H}_2\text{O}_2]$ is similarly dependent on k_{22} but not on k_{11} .

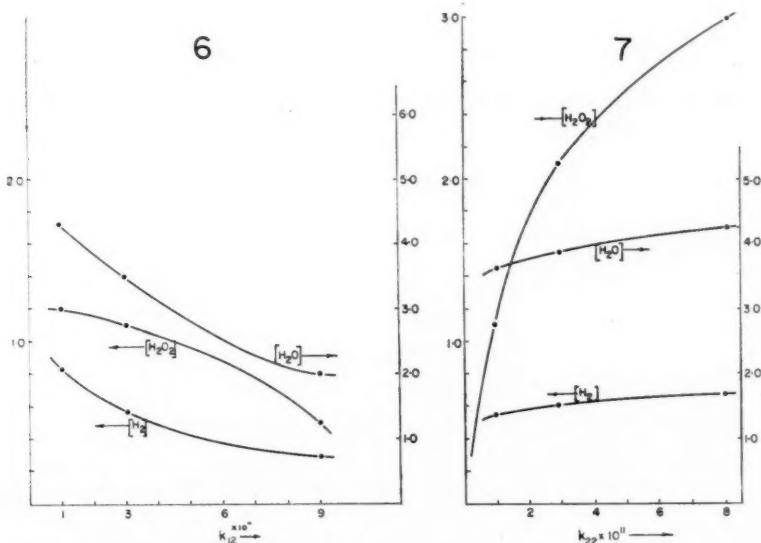


FIG. 6. Variation of yields with the values of k_{12} . Cases (A), (I), and (J).

FIG. 7. Variation in yields with a value of k_{22} . Cases (A), (K), and (L).

9. YIELDS AS A FUNCTION OF SPUR SIZE AND THE NUMBER OF RADICALS PER SPUR

There are two ways in which the variation of yield with the size of the spur can be examined. Either the relative size of the two distribution functions for the radicals or the size of both distributions may be changed. Owing to the "hot atom" effect the hydrogen atoms may be more widely dispersed than the hydroxyl radicals, i.e. $R_1 > R_2$,

where R_1 and R_2 are the characteristic radii for H atoms and OH radicals respectively. Variation of R_1 , keeping R_2 constant, is followed in (Y) and (Z) and the results are plotted in Fig. 8. As R_1 is increased $[H_2]$ decreases and both $[H_2O_2]$ and $[-H_2O]$ increase.

The yields as a function of both radical distributions are followed in (S) and (T). Values of $f(H_2)$ and $f(H_2O_2)$ derived from these cases are shown in Fig. 9; they are rapidly

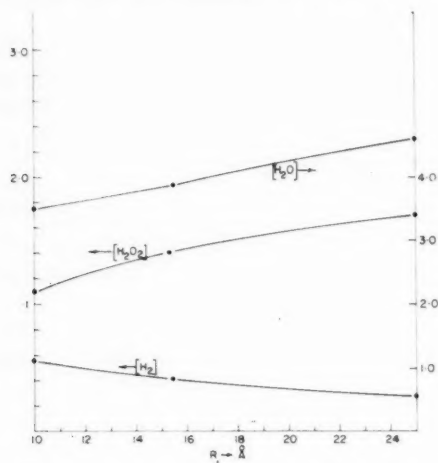


FIG. 8. Variation in yields with R_1 , R_2 being unchanged. Cases (A), (Y), and (Z).

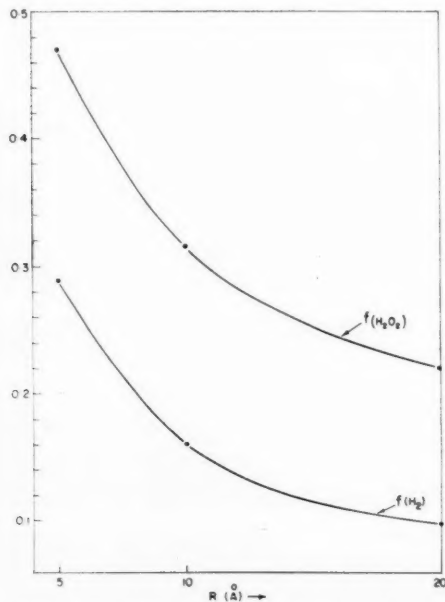


FIG. 9. Variation of $f(H_2)$ and $f(H_2O_2)$ as a function of the over-all spur size, i.e. $R_1 = R_2$. Cases (A), (S), and (T).

varying functions of size particularly for small values of the "radius". Yields as a function of the number of radicals per spur are shown in Fig. 10 for spurs of constant size ($R = 10 \text{ \AA}$) and for spurs of varying size determined by the relation $R\alpha(N)^{1/3}$, a radius of 10 \AA being taken for the spur with $N = 6$. These latter values were obtained by interpolation from the changes in $f(\text{H}_2)$ and $f(\text{H}_2\text{O}_2)$ with R shown in Fig. 9. For example, the cube-root relation gives $R = 11.5 \text{ \AA}$ when $N = 9$. From Fig. 9 we calculate the ratio of $f(\text{H}_2)$ at 10 \AA to that at 11.5 \AA and decrease the value of $f(\text{H}_2)$ for $N = 9$ by this ratio. This treatment assumes that these ratios (calculated for $N = 6$) are independent of N . This assumption was checked with a spot calculation for $N = 15$ with $R = 20 \text{ \AA}$. The calculation gave $f(\text{H}_2) = 0.22$ and $f(\text{H}_2\text{O}_2) = 0.39$. The interpolation technique gave $f(\text{H}_2) = 0.23$, $f(\text{H}_2\text{O}_2) = 0.38$.

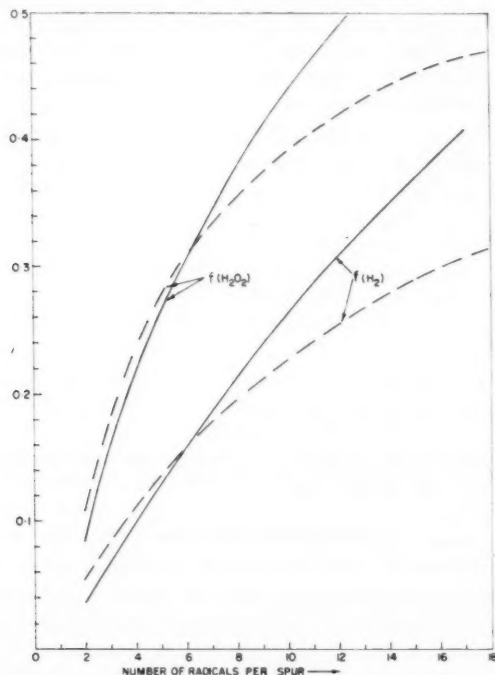


FIG. 10. Variation in $f(\text{H}_2)$ and $f(\text{H}_2\text{O}_2)$ with N , the number of radicals per spur. The full lines refer to spurs of constant size $R = 10 \text{ \AA}$. In the broken line values of $f(\text{H}_2)$ and $f(\text{H}_2\text{O}_2)$ are shown in which R varies as $\sqrt[3]{N}$ assuming that $R = 10 \text{ \AA}$ when $N = 6$. Cases (A), (U), (V), (W), and (X).

The parameters N and R are, in a sense, complementary. If the k 's and D 's are fixed, we can always find values of R for any value of N which will give the experimental value of $f(\text{H}_2)$ or of $f(\text{H}_2\text{O}_2)$. This is illustrated in Fig. 11, where the solid line gives the values of N and R which give $f(\text{H}_2) = 0.24$; the values were determined by interpolation as described in the last paragraph. The solid line corresponds to the choice of k 's and D 's made in (A). Another line would be generated by a different choice. For instance from Fig. 3 we find that $N = 6$, $R = 10 \text{ \AA}$, $k_{12} = 5.2 \times 10^{-10}$, $k_{11} = 2.1 \times 10^{-11}$, $k_{22} = 1.5 \times 10^{-11}$ would also give $f(\text{H}_2) = 0.24$. This defines the circled point in Fig. 11. We can derive another line also defining $f(\text{H}_2) = 0.24$ going through this point. This is indicated by the

broken line and which is again obtained by interpolation. It does not matter for this argument whether or not this interpolation is exact. The point is that a whole family of lines exists describing spurs with $f(\text{H}_2) = \text{a constant}$. By interpolation from Figs. 5 and 6 two other sets of k 's can be found which would generate lines essentially coincident with the dotted line. These are: $k_{12} = 3.0 \times 10^{-11}$, $k_{11} = 1.7 \times 10^{-11}$, $k_{22} = 0.9 \times 10^{-11}$ and $k_{12} = 0.5 \times 10^{-11}$, $k_{11} = 1.2 \times 10^{-11}$, $k_{22} = 0.9 \times 10^{-11}$.

The plot in Fig. 11 illustrates the fact that we can, with our present information, make no unique choice of constants which will give agreement with experiment. Plots similar to Fig. 11 could be constructed for $f(\text{H}_2\text{O}_2)$ and $[-\text{H}_2\text{O}]$ which would restrict our choice from the larger number allowed by Fig. 11. Such a search would not be very useful. Instead we choose to pick out parameters which, if fixed, would give the most valuable information for the model. The two most important parameters from this point of view are the spur size or volume and the number of radical pairs per spur. It is quite clear from Fig. 11 that the model will only work for small spurs where the characteristic length R is less than 20 \AA . The figure $R = 10 \text{ \AA}$ was, in fact, originally chosen by Samuel and Magee to give agreement with experiment.

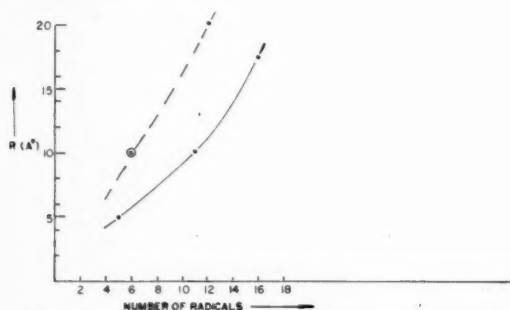


FIG. 11. Values of R , the radii, and N , number of radicals per spur, for which $f(\text{H}_2) = 0.24$. The solid line refers to the choice of k 's and D 's made in (A). The dotted line refers to several choices of k 's which for $N = 6$ and $R = 10 \text{ \AA}$ also give $f(\text{H}_2) = 0.24$.

10. ISOTOPE EFFECTS

Several workers have shown that (11, 12, and 13) the yield of deuterium gas from acidic solution in heavy water is about 25% less than the yield of hydrogen from the corresponding light water solutions. It is also known that the yield of the ferrous sulphate dosimeter is increased in heavy water solutions (14). If the stoichiometry for the oxidation of ferrous ion in light water is assumed to hold in heavy water these two observations show that, in $0.8 N \text{ H}_2\text{SO}_4$, $G(-\text{D}_2\text{O})$ is greater than $G(-\text{H}_2\text{O})$. Yields of hydrogen gas and hydrogen atoms and OH radicals and their deuterium analogues have been measured by Burton and Phung (13) in neutral solutions using benzene as a scavenger. They find that all the yields are lower than the corresponding yields in light water. The results are shown in Table III.

Burton and Phung point out that these results are not consistent with those of other workers, as may be seen by comparing Table III with Table II.

For this discussion the problem of isotope effects may be stated as follows, "Under what circumstances does the diffusion model predict a lower value of $G(\text{D}_2)$ coupled with (a) an increased value of $G(-\text{D}_2\text{O})$ or (b) a decreased value of $G(-\text{D}_2\text{O})$?" Following the arguments which are used in Section 4 to establish the initial choice of constants,

TABLE III
 PRIMARY YIELDS IN THE RADIOLYSIS OF LIGHT AND HEAVY WATER

| | $G(\text{H}_2)(\text{D}_2)$ | $G(\text{H}_2\text{O}_2)(\text{D}_2\text{O}_2)^*$ | $G(\text{OH})(\text{OD})$ | $G(\text{H})(\text{D})$ | $G(-\text{H}_2\text{O})(-\text{D}_2\text{O})$ |
|-------------|-----------------------------|---------------------------------------------------|---------------------------|-------------------------|-----------------------------------------------|
| Light water | 0.41 | 0.61 | 2.64 | 3.04 | 3.86 |
| Heavy water | 0.32 | 0.51 | 2.38 | 2.76 | 3.40 |

*The yield of peroxide is determined from stoichiometry.

the constants for heavy water are obtained by reducing D_1 to $1/\sqrt{2}$ of its value in (A) and adjusting k_{11} and k_{12} in accordance with the Smoluchowski relation (Section 4). This gives $k_{11} = 8.48 \times 10^{-12}$, $k_{12} = 2.296 \times 10^{-11}$, and $D_1 = 5.657 \times 10^{-8}$. These are the new constants for (M). It will be noted that the yields in (M) are identical with those of (A). The variation of constants required by "simple" theory produces no isotope effect. The qualitative explanation of this is that the change in k_{11} and k_{12} introduced in (M) compensates exactly for the slower diffusion of H atoms which would otherwise result in increased $[\text{H}_2]$ and $[\text{H}_2\text{O}^*]$ yields.

As the isotope effects are not explained by the "simple" choice of constants some special variation of one or more of them must be postulated. An obvious way of reducing the yield of molecular hydrogen would be to suppose that $k_{\text{D}\text{D}}/k_{\text{H}\text{H}} < 1/\sqrt{2}$. The effect of variation of k_{11} is shown in Fig. 5 and it is noted that a change in k_{11} required to reduce $[\text{H}_2]$ by $\frac{1}{4}$ leaves $[\text{H}_2\text{O}_2]$ virtually unchanged and decreases $[-\text{H}_2\text{O}]$ only slightly.

A decrease in $[-\text{H}_2\text{O}]$ could be explained by invoking the hot atom effect. As the displacement of the D atom on the dissociation of the excited D_2O molecule will be smaller than the corresponding displacement of an H atom it follows that the characteristic radii for these atoms will be different, i.e. $R_1(\text{H}) > R_1(\text{D})$. An inspection of Fig. 8 shows that a relatively large change in R_1 , of the order of 80%, is required to make the required decrease in $[\text{H}_2\text{O}_2]$ and $[-\text{H}_2\text{O}]$. This does not seem likely. It would also be necessary to postulate a further change in k_{11} large enough to affect the increase in the D_2 yield owing to the smaller characteristic radius for the deuterium atoms. A special variation in k_{11} does not therefore explain the results obtained in acidic heavy water solution and is not a very convincing explanation of the results obtained with benzene scavengers.

A choice of constants which would give a simultaneous decrease in all the molecular yields and radical yields is shown in (N). In this case both k_{11} and D_1 are smaller by a factor of two than they are in (A). k_{12} and all the other parameters are unaltered. The calculation shows that all the yields except $[\text{H}_2\text{O}^*]$ are smaller than they are in (A). When D_1 is reduced the H atoms are confined for a longer time to the region where the concentration of OH is high. $[\text{H}_2\text{O}^*]$ is therefore increased and $[-\text{H}_2\text{O}]$ is decreased. This removal of H atom and OH radicals from the central region in turn reduces $[\text{H}_2]$ and $[\text{H}_2\text{O}_2]$.

Now according to the Smoluchowski equation (Eq. [3]) k_{12} should be smaller if D_1 is smaller. By giving k_{12} the same value as in (A) we are in effect making it larger than it would be with a "simple" choice of constants. In other words a change in yields parallel to that found by Burton and Phung is obtained by increasing k_{12} . The variation of yields with k_{12} is shown in Fig. 6 and demonstrates graphically the reduction in $[\text{H}_2]$, $[\text{H}_2\text{O}_2]$, and $[-\text{H}_2\text{O}]$.

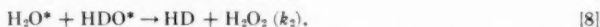
This explanation of the isotope effect in neutral solution is of interest because the arguments of Section 12 suggest that k_{12} is relatively greater in D_2O than in H_2O owing to differences in the initial spatial configuration of the radicals.

No simple variation in constants is apparent which will explain a decrease in $[H_2]$ coupled with an increase in $[-H_2O]$, as found in acid solutions. Speculations on this topic must be deferred until more detailed information on the yields in acid solutions is available. In any case the simple diffusion theory which neglects any effect of hydrogen ions and the intervention of such species as H_2^+ is not applicable to a discussion of acidic solutions.[†]

A second type of isotope effect is observed in the isotopic composition of molecular hydrogen evolved from dilute solution of heavy water. This has been studied by Kelly, Rigg, and Weiss (15), who measured the separation factor.

$$S = [H_2/HD]_{\text{gas}}/[H_2O/HDO]_{\text{water}} \approx [HDO]/[H_2]/[H_2O]/[HD] \quad [6]$$

for solution containing about 1 mole % deuterium and various scavengers. Deaerated ferrous sulphate solution gave $S \approx 3.5$, close to the value of 3.8 for thermal equilibrium at room temperature. Solutions which contained efficient scavengers for hydrogen atoms, e.g. oxygen saturated ferrous sulphate and deaerated ceric sulphate, gave $S \approx 2$. It was suggested that the hydrogen evolved from deaerated ferrous sulphate was thermally equilibrated but with solutions giving lower separation factors, exchange and equilibration were not taking place. Kelly, Rigg, and Weiss suggested that the hydrogen was produced by reactions involving excited molecules.



The separation factor will be given by the ratio k_1/k_2 . In their second publication (15b) Kelly, Rigg, and Weiss suggest that $k_1/k_2 \approx 2$ owing to the difference in activation energy of the two reactions. A difference of 0.4 kcal, attributed to the different zero-point energies of H_2O , HDO , is postulated.

We have calculated the extent of recombination of H and D atoms in a spur to give H_2 , HD, and D_2 and hence determined the separation factors predicted by the model. On "simple" assumptions the model gives $S = 1$, i.e. no separation.

Consider the statistics of the formation of HD from a spur containing $(n-1)$ H atoms and one D atom. Neglecting isotope effects in the rate constants the probability of forming an HD molecule is proportional to $(n-1)$, and the probability of forming an H_2 molecule is $(\frac{1}{2})(n-1)(n-2)$. The fraction of HD is $[HD]/([H_2] + [HD]) = 2/n$ of the total "hydrogen" produced in the spur. If the aqueous phase contains $p\%$ HDO (p is ≈ 1) then the percentage of spurs containing one HDO molecule is np . If the HDO dissociates statistically (this is discussed later) the percentage of spurs containing one D atom is $np/2$. The composition of all the evolved hydrogen is therefore $2/n \times np/2 = p\%$ HD and the separation factor is unity.

Isotope effects in the recombination and diffusion processes can be neglected because in the Samuel-Magee model, changes in rate constants and diffusion constants work in opposition to one another. We have used the "two radical" calculation to estimate the relative probabilities of recombination of H and D atoms in spurs containing six atoms in all. Putting $D_1 = 8 \times 10^{-5}$, $D_2 = 5.656 \times 10^{-5}$, $k_{11} = 1.2 \times 10^{-11}$, $k_{12} = 2.040 \times 10^{-11}$, and $k_{22} = 8.484 \times 10^{-12}$ and with spurs with $N_1 = 5$, $N_2 = 1$ and $N_1 = 1$, $N_2 = 5$ we find yields of $[H_2] = 0.68$ and $[HD] = 0.32$ and $[D_2] = 0.68$ and $[HD] = 0.32$, respectively. The numerical identity justifies the neglect of isotope effects and is in agree-

[†]Note added in proof: A discussion of molecular and radical yields in D_2O which complements the present discussion has been given by Armstrong, Collinson, and Dainton, *Proceedings of Second Conference on Peaceful Uses of Atomic Energy*, P/1517.

ment with the statistical ratio of $2/n = \frac{1}{3}$ for the fraction of HD in a six-radical spur.

Two tacit assumptions have been made in this discussion, firstly that hydrogen and deuterium atoms are produced, "statistically", with equal probability from an HDO molecule and secondly that no exchange reactions of the type $H + HD \rightarrow H_2 + D$ occur in the track when scavengers are present. Calculation of these 'secondary' exchange reactions would require a more elaborate computation procedure. We note that rate constants for these exchange reactions are two to three orders of magnitude smaller than the rate constants for recombination and on this basis the amount exchange which would occur in the lifetime of the spur (10^{-8} seconds) would be small.

Mass spectral data on isotopically substituted molecules such as CH_3D show that the deuterium atom is 'more firmly' held than any one hydrogen atom by a factor of two or more (16). The theoretical interpretation of these results is general and predicts in principle the same effect for HDO, i.e. the dissociation.



might be about twice as probable as



Such a difference would, in the present case, reduce the number of spurs containing a D atom below the value predicted statistically and would give a separation factor greater than unity as was found experimentally by Kelly, Rigg, and Weiss.

This difference would lead to a value of less than unity for the separation factor.

$$S' = [D_2/HD]_{gas}/[D_2O/HDO]_{liq} = [HDO][D_2]/[D_2O][HD]$$

describing the isotopic separation of gas evolved from dilute solution of HDO in D_2O containing scavengers. A value of 0.54 has been found experimentally in this laboratory for this system with the scavengers used by Kelly, Rigg, and Weiss.

The preferential dissociation of HDO to $H + OD$ also explains the G -values found by Bardwell and Dyne (17) for the radiation-induced exchange of hydrogen atoms between liquid water and dissolved hydrogen. The exchange was followed by a tracer technique using H_2O containing about 1% HDO. The total amount of the exchange was calculated assuming that HDO dissociated statistically. This was between $\frac{1}{2}$ and $\frac{1}{3}$ of that found by Gordon and Hart (18), who studied the system D_2 , H_2O and who were consequently able to detect directly every exchange.

11. THE EFFECT OF SCAVENGER CONCENTRATION

If the concentration of scavenger is increased the yields of molecular products decrease slowly. This effect (19, 20, 21), which has been extensively studied experimentally and theoretically, is due to competition between the scavenging process and the recombination process during the time in which the latter is proceeding at a significant rate.

The scavenger effect is calculated by varying the terms $k_{1s}C_s$ and $k_{2s}C_s$. A plot of the relative yields against C_s refers only to the particular choices of k_{1s} ; if k_{1s} were larger than that chosen then the same decrease in yield would be observed at a correspondingly smaller value of C_s . The relative yields plotted in Fig. 12 were obtained with $k_{1s} = k_{2s} = 1 \times 10^{-11}$. It is found that the $[H_2]$ yield is less sensitive to scavenger than the $[H_2O_2]$ yield.

This arises because we have put $k_{1s} = k_{2s}$. Because of the greater diffusion constant of the H atom k_{1s} will be larger than k_{2s} with the practical result that the effects of

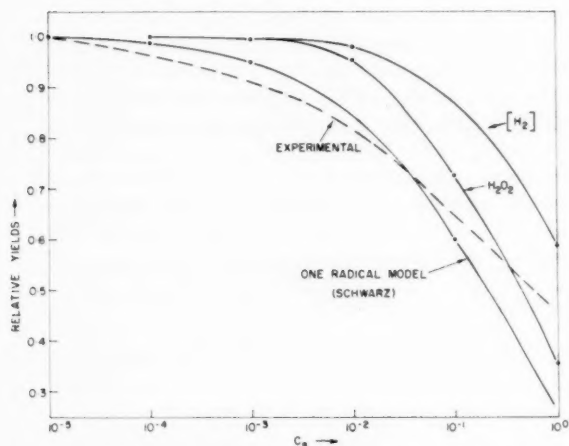


FIG. 12. Variation in relative yields with the scavenger concentration. The curves labelled H_2 , H_2O_2 are from the present calculation. The calculated one radical model curve and the experimental curve are taken from Schwarz (19). Cases (A), (O), (P), (Q), and (R).

scavenger on $[H_2]$ and $[H_2O_2]$ will be more nearly equal.* Using the Smoluchowski equation to estimate the relative values of k_{1s} and k_{2s} we conclude that k_{1s} would be two or three times greater than k_{2s} . A calculation has shown that, at a concentration of $10^{-1} M$ with $k_{1s} = 3.0 \times 10^{-11}$ and $k_{2s} = 1.0 \times 10^{-11}$ the change in relative yields for $[H_2]$ and $[H_2O_2]$ are identical and fall on the curve for $[H_2O_2]$.

A theoretical curve calculated by Schwarz (19) is also shown in Fig. 12 together with an experimental curve. The theoretical curve was calculated analytically using a simplified one-radical model. The curve was adjusted by altering the scale on the concentration axis so that it coincided with the experimentally determined curve for the variation of $[H_2]$ with nitrite as scavenger. Schwarz showed that the data for both hydrogen and hydrogen peroxide yields for a variety of scavengers lay on similar curves. These curves could be brought into coincidence by multiplying the concentration by an empirical normalizing constant, which gives, in effect, the value of k_s relative to that for nitrite. These relative values were shown to be in agreement with experiment. The experimental curve in Fig. 12 is a curve which we have drawn from points plotted by Schwarz.

At large scavenger concentrations the experimental decrease in yield is less than that predicted. This is due to the assumption that C_s is a constant both in time and space. For $C_s = 1$ molar our numerical calculations show that three out of six radicals have reacted with scavenger in about 10^{-11} seconds. In this short time the spur has not expanded appreciably by diffusion and its effective volume is still $(10^{-7} \text{ cm})^3 = 10^{-21} \text{ cm}^3$. This volume contains less than one scavenger atom at a concentration of 1 M . It follows that there is a depletion of scavenger at high scavenger concentration inside the volume of the spur and the decrease in yield will be less than that predicted on the assumption that C_s is a constant.

At low scavenger concentrations the new theoretical curves and that given by Schwarz show a smaller decrease in yield than is observed experimentally. As this amounts to only 10%, this discrepancy may fairly be attributed to some of the simplifications

*We are indebted to Dr. H. Schwarz for clarification on this point.

inherent in our treatment of the model. The nature of one of these simplifications can be seen in calculations on the same effect by Ganguly and Magee (21). They used a one-radical model but took into account the effects of overlap of spurs. This becomes more significant as the energy of the primary β -particle is decreased; for β -particles of 0.01 Mev energy a curve is obtained which falls steadily as the concentration of scavenger is increased instead of having an initial flat portion for concentrations up to 10^{-3} M. The curves calculated by Ganguly and Magee are not, unfortunately, reproduced in sufficient detail to permit a detailed comparison. The present calculations and those of Schwarz apply to spurs generated by high energy β -particles; which are so far apart that they never overlap significantly.

The curve calculated by Schwarz was adjusted to give agreement with experiment; no a priori assumptions being made as to the value of k_s . From the figure it can be seen that k_s must be $\sim 10^{-10}$ rather than $\sim 10^{-11}$ for there to be agreement between theory and experiment. Rate constants of $\sim 10^{-10}$ are approaching the values given by the kinetic theory for gas-phase reactions. Most of the normalization constants given by Schwarz are of the order of unity or somewhat larger and values of k_s are correspondingly smaller, i.e. $3-5 \times 10^{-11}$.

The fact that the experimental yields for hydrogen and hydrogen peroxide lie on one curve (Fig. 12) is good evidence that they are formed by a similar process. The agreement between the experimental and theoretical curves is again evidence that this process is a bimolecular one, occurring in a diffusion-controlled scheme of the type proposed by Samuel and Magee and which is in competition with a scavenging reaction. This evidence does not however prove that the bimolecular processes are recombinations of hydrogen atoms and hydroxyl radicals; similar experimental curves would be obtained if, for instance, the products were formed by $2\text{H}_2\text{O}^* \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$ and if the excited water molecule H_2O^* reacted with the scavenger to give other products.

12. A CRITICISM OF THE MATHEMATICAL CONSTRUCTION OF THE MODEL

The equations [1] and [2] used in these calculations apply the concepts of classical chemical kinetics to reactions occurring in small volumes containing only a few molecules and occurring in very short times which are of the order of magnitude of the time between molecular jumps in a liquid. The equations deal with spatial distributions of concentration which are expressed as a continuous analytic function of the co-ordinates—no account being taken of the movements of individual radicals. A treatment of the process as a form of "random walk" is clearly more appropriate and this could conceivably be handled with a large enough computer. Leaving aside the last practical difficulty, it is difficult to devise a molecular model for the diffusion and reaction of molecules in liquid water which is not open to objections as serious as those placed against the analytical treatment. In particular the results of a random walk treatment depend on the way in which, say, the spatial movements are defined; whether the directions are random or whether some directions are preferred, whether the distances in one jump are constant or variable, etc. It is as difficult to estimate the errors involved in making assumptions of this type as it is to estimate the errors in the use of the diffusion approximation.

The model, as used in this paper, does not take into account the possible correlations in the spatial distributions of the particles. As the excited water molecules, the parents of the reactive radicals are generated along the random path of a slow electron it is proper to describe the spatial distribution of these water molecules by a distribution function which is equivalent to a concentration. The spatial distribution of the H and

OH radicals which originate from these excited water molecules will also be described by this or some similar concentration function and these functions are appropriate for calculating the probabilities of recombination $k_{11}C_1^2$, $k_{22}C_2^2$. They are not, however, necessarily applicable to the evaluation of the term $k_{12}C_1C_2$ because each hydrogen may be, on the average, much closer to the OH radical which was its original partner than it is to the nearest other hydrogen atom. In other words there is a correlation between the concentrations C_1 and C_2 . In terms of the mathematical techniques used here this means that k_{12} is not a true rate constant as it will vary with time. In the case of extreme correlations between like particles k_{12} in equation [1] and [2] is initially much greater than the kinetic theory rate constant for the reaction $H + OH \rightarrow H_2O$. This is of interest in connection with the isotope effect where in section 10 we suggested that k_{12} was larger for the reaction $D + OD \rightarrow D_2O$ than it was for $H + OH \rightarrow H_2O$. The "constant" k_{12} depends initially on the separation between two radicals H, OH and D, OD. Because of the large relative difference in the masses of H and D atoms this may be significantly different. The isotope effect may be attributed to differences in the correlation functions, which are expressed in the term k_{12} .

If there is a very large correlation between H and OH, i.e. the initial separation between the dissociated atoms is small, then it follows that there is a high probability of these radicals recombining and they never really contribute to the initial number of radicals in the spur. For this reason the value of $G(-H_2O)$ given by Firestone for water vapor represents an upper limit for the initial amount of decomposition in the liquid water.

Monchick, Samuel, and Magee (8) have published a brief set of calculations on a two-radical model which includes a treatment of the correlation term. Their treatment is approximate and no significant differences are noticeable between their yield values and those obtained in these calculations which are approximate in the sense that k_{12} is taken as a constant.

In this paper we have examined the Samuel-Magee model pragmatically and have accepted its premises about primary processes in the spur without question. The model leads to reasonable interpretations of the experimental data but, with the exception of experiments on the isotope effects, it is not sufficiently well defined to allow any very critical tests. In the relatively restricted field of study we have not found any experimental data which the model cannot explain nor have we found any evidence for any "new" primary processes. Our numerical data have been presented so that they may suggest more decisive experiments and so that, when new data are available, the qualitative effect on the model can be readily estimated.

ACKNOWLEDGMENTS

We take pleasure in acknowledging the assistance of Mrs. Arden Okazaki in the writing of the detailed computer program and the benefit of many stimulating discussions with Dr. R. W. Attree, Dr. R. H. Betts, and Dr. Boris Davison.

APPENDIX

THE NUMERICAL METHOD

1. Analytical Transformations

The original equations for the concentrations C_1 and C_2 are

$$\partial C_i / \partial t = D_i \nabla^2 C_i - k_{id}[(N_i - 1)/N_i]C_i^2 - k_{12}C_1C_2 - k_{1s}C_iC_s \quad [1]$$

for $i = 1, 2$. The k_{ij} are rate constants, and N_i the total number of particles in the system

$$N_i(t) = \int C_i(r,t) dV. \quad [2]$$

By convention, the particles are labelled so that D_1 is the larger of the two diffusion constants.

Three transformations are applied to the variables:

(a) A dimensionless space variable $\rho = r/\sqrt{(D_1 t)}$ is defined in order that a fixed range in ρ corresponds to an expanding range in r as time proceeds. This is to keep pace with the outward diffusion of the particles.

(b) A dimensionless time variable $x = \log(t/t_0)$ is used to take account of the fact that the phenomenon can be examined on an expanded time scale as time proceeds. The choice of the initial time t_0 is discussed below.

(c) New dependent variables are defined by

$$Y = \rho C_1; \quad Z = \rho C_2. \quad [3]$$

These effectively transform the spherical geometry to plane geometry and simplify the equations.

The final form becomes

$$\begin{aligned} \frac{\partial Y}{\partial x} &= \left[\frac{\partial^2 Y}{\partial \rho^2} + \frac{\rho}{2} \frac{\partial Y}{\partial \rho} + \frac{Y}{2} \right] - \frac{k_{11} t_0 e^{-x/2} Y^2}{\rho} - \frac{k_{12} t_0 e^{-x/2} YZ}{\rho} - k_{13} t_0 e^x C_S Y, \\ \frac{\partial Z}{\partial x} &= \left[\Delta \frac{\partial^2 Z}{\partial \rho^2} + \frac{\rho}{2} \frac{\partial Z}{\partial \rho} + \frac{Z}{2} \right] - \frac{k_{22} t_0 e^{-x/2} Y^2}{\rho} - \frac{k_{12} t_0 e^{-x/2} YZ}{\rho} - k_{23} t_0 e^x C_S Z, \end{aligned} \quad [4]$$

where $\Delta = D_2/D_1$.

2. Numerical Method

The problem is the integration of the pair of equations [3] from $x = 0$, given the initial spatial distributions

$$C_i(r,0) = [N_i(0)\beta^3/\pi^{3/2}]e^{-\beta^2 r^2}. \quad [5]$$

The space dependence is handled by replacing the functions $Y(\rho)$ and $Z(\rho)$ at any time by 40-place tables Y_n, Z_n for $\rho = nh$ ($n = 0, 1, \dots, 39$). The derivatives are then replaced by

$$\begin{aligned} \partial^2 Y_n / \partial \rho^2 &= (Y_{n+1} - 2Y_n + Y_{n-1})/h^2, \\ \partial Y_n / \partial \rho &= (Y_{n+1} - Y_{n-1})/2h, \end{aligned} \quad [6]$$

and the corresponding results for Z . Thus the system reduces to 80 simultaneous first-order ordinary differential equations for the Y_n and Z_n .

Because of the definitions [3], the conditions $Y_0 = Z_0 \equiv 0$ are imposed. At the outer boundary, we set $Y_{39} = Z_{39} \equiv 0$; this implies that h is sufficiently large that no appreciable error arises from confining the phenomenon to a finite volume.

The integration in time proceeds by a step-by-step process, correct to second order in Δx . A "mid-point" procedure is used to make the evaluation of the right-hand sides necessary only once per interval.

3. The Input Data

The problem is defined by a choice of k_{11} , k_{22} , k_{12} , $k_{1S}C_S$, $k_{2S}C_S$, $N_1(0)$, $N_2(0)$, β_1 , β_2 , D_1 , and Δ . In addition, t_0 , h , and Δx must be chosen according to criteria imposed by the physics of the problem.

t_0 must be the time appropriate to the expansion of a δ -function distribution to the distribution given by $C_1(r, 0)$ when the diffusion constant is D_1 ; otherwise the expansion of the spatial co-ordinate will fail to keep pace with the phenomenon at subsequent times. In practice, $t_0 = \frac{1}{6}\beta_1^2 D_1$ has been used. The theoretical value, $t_0 = \frac{1}{4}\beta_1^2 D_1$ leads to an incipient instability in the mathematical treatment.

Once t_0 is chosen, the space interval h must be chosen to make the initial range of r contain all significant parts of the initial Gaussian distributions. If h is too small, the imposition of the outer boundary condition introduces errors that become magnified as time progresses; if it is too large, accuracy is lost through failure to make good use of the full 40-entry tables. With the given choice of t_0 , a satisfactory value of h is 0.3.

Finally, Δx must be small enough to give reasonable accuracy in the time integrations. Experience has shown that $\Delta x = 0.22$ is reasonable for the cases run so far. An instability in the solution appears rather suddenly above $\Delta x = 0.25$.

4. Output

At the end of every step, the computer accumulates the losses of particles L_{ij} owing to each of the five recombination terms and recalculates N_1 and N_2 . After every fifth or tenth step, the following information is printed:

Elapsed time:

| | | | | |
|----------|----------|----------|-------|--------------------|
| L_{11} | L_{12} | L_{1S} | N_1 | (sum) ₁ |
| L_{22} | L_{2S} | L_{2S} | N_2 | (sum) ₂ |

The elapsed time is $T = t_0(e^x - 1)$. The sums should remain equal to $N_1(0)$ and $N_2(0)$, within the accuracy of the calculation.

REFERENCES

1. SAMUEL, A. H. and MAGEE, J. L. *J. Chem. Phys.* **21**, 1080 (1953).
2. DEWHURST, H. A., SAMUEL, A. H., and MAGEE, J. L. *Radiation Research*, **1**, 62 (1954).
- 3(a). ORR, W. J. C. and BUTLER, J. A. V. *J. Chem. Soc.* 1273 (1935).
- (b). WANG, J. H., ROBINSON, C. V., and EDELMAN, I. S. *J. Am. Chem. Soc.* **75**, 466 (1953).
4. FRICKE, H. *Ann. N.Y. Acad. Sci.* **59**, 567 (1955).
5. WILSON, C. T. R. *Proc. Roy. Soc. (London)*, **A**, **104**, 192 (1923).
6. BEEKMAN, W. J. *Physica*, **15**, 327 (1949).
7. FIRESTONE, R. F. *J. Am. Chem. Soc.* **78**, 3226 (1956); **79**, 5593 (1957).
8. MONCHICK, L., MAGEE, J. L., and SAMUEL, A. H. *J. Chem. Phys.* **26**, 935 (1957).
9. ALLEN, A. O. *Disc. Faraday Soc.* No. 12, 79 (1952).
10. ALLEN, A. O. *Radiation Research*, **1**, 85 (1954).
11. HART, E. J., McDONELL, W. R., and GORDON, S. *Intern. Conf. on the Peaceful Uses of Atomic Energy*, **7**, 576 (1955).
12. HARDWICK, T. J. Private communication.
13. PHUNG, P. V. and BURTON, M. *Radiation Research*, **7**, 199 (1957).
14. TRUMBORE, C. N. and VAN ATEN, A. H. W. *J. Am. Chem. Soc.* **78**, 4179 (1956).
15. KELLY, P., RIGG, T., and WEISS, J. (a) *Nature*, **173**, 1130 (1954); (b) *Chemistry & Industry*, 1291 (1954).
16. FIELD, F. H. and FRANKLIN, J. L. *Electron impact phenomena*. Academic Press Inc., New York, 1957. pp. 204-217.
17. BARDWELL, J. and DYNE, P. J. *Can. J. Chem.* **35**, 82 (1957).
18. GORDON, S. and HART, E. J. *J. Am. Chem. Soc.* **77**, 3981 (1955).
19. SCHWARZ, H. A. *J. Am. Chem. Soc.* **77**, 4960 (1955).
20. SWORSKI, T. J. *J. Am. Chem. Soc.* **76**, 4687 (1954); *Radiation Research*, **2**, 26 (1955).
21. GANGULY, A. K. and MAGEE, J. L. *J. Chem. Phys.* **25**, 129 (1956).

FATTY ACIDS OF THE SEED OIL OF *CARDIOSPERMUM HALICACABUM*¹

MARY J. CHISHOLM AND C. Y. HOPKINS

ABSTRACT

The seed oil of *Cardiospermum halicacabum* L., family Sapindaceae, was found to have 11-eicosenoic acid as the major fatty acid in its glycerides. In this respect it is unique among the true natural fats. The amount of eicosenoic acid in the sample examined was 42% of the total long-chain fatty acids. The identity and amounts of the principal fatty acids of the oil were determined by gas chromatography and by distillation of the methyl esters. The estimated percentages were: palmitic 3, linolenic 8, linoleic 8, oleic 22, stearic 2, eicosenoic 42, arachidic 10. In addition, there was evidence of small proportions (1-2%) of a low-molecular-weight acid and of C₂₂ acids.

In studying the occurrence of eicosenoic acid in seed oils, attention was directed to the family Sapindaceae. An unsaturated C₂₀ acid has been reported as a minor component in the seed oil of three species of this family, although the acid was not completely identified in these instances (5, 6, 7).

Most of the Sapindaceae are found in tropical and subtropical regions but one genus, *Cardiospermum*, grows also in temperate climates. *Cardiospermum halicacabum* (balloon vine) was chosen for study. A previous analysis of its seed oil showed the presence of arachidic acid but not of unsaturated C₂₀ acid (3). It was surprising, therefore, to find in the present work that the sample gave an oil in which 11-eicosenoic acid constituted 42% of the total fatty acids.

The other acids of the oil also differed in some respects from those of the more common seed oils.

EXPERIMENTAL

Properties of the Oil

Seed of *Cardiospermum halicacabum* L., originating in Holland, was obtained from a commercial seed house. The spherical seeds had an average weight of 0.074 g and were easily ground. The yield of oil, by extraction with petroleum ether, was 28.0% on a 10% moisture basis. Constants of the oil are shown in Table I.

TABLE I
PROPERTIES OF THE OIL

| | | | |
|--------------------------|------|-----------------------|----------|
| Iodine value | 86.8 | Acetyl value | 0.9 |
| Saponification value | 206 | Refractive index, 25° | 1.4709 |
| Unsaponifiable matter, % | 0.4 | Halphen test | Negative |
| Acid value | 11.7 | | |

Composition of the Fatty Acids

A sample of the oil was saponified, freed from unsaponifiable matter, and converted to methyl esters. During the removal of the solvent, after esterification, esters of any short-chain acids are volatilized. The analysis is therefore restricted to the longer-chain acids.

¹Manuscript received July 29, 1958.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4767.

The esters were examined by gas chromatography, using a Perkin-Elmer fractometer, model 154-B. The detector was a thermistor type thermal conductivity cell. The column was 1 meter in length and was packed with Apiezon M stopcock grease on Celite. It was operated at 225° with a helium flow rate of 95 ml/minute at an inlet pressure of 15 p.s.i.

The proportions of the chief components were estimated from the chromatogram (Fig. 1) by chain length as follows: C_{16} 3, C_{18} 41, C_{20} 52. In addition there were minor peaks (not shown) indicating about 2% of a low-molecular weight acid and about 2% of C_{22} acid(s).

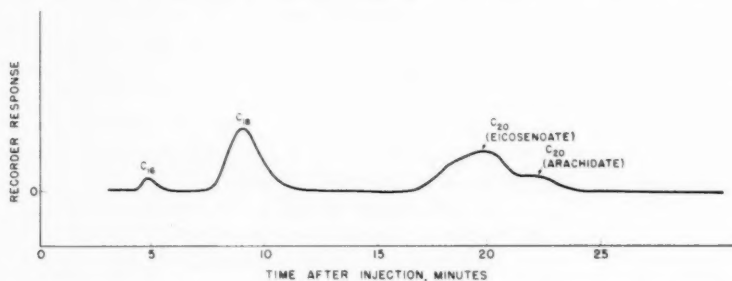


FIG. 1. Main portion of the gas chromatogram of the methyl esters. The peaks represent esters of C_{16} , C_{18} , and C_{20} acids.

A sample of the mixed esters was isomerized by alkali (45 minutes at 180° in glycerol) and examined by ultraviolet absorption. The results showed a content of 8.0% of dienoic acid and 7.6% of trienoic acid, calculated as octadecoic acids. A sample of the mixed fatty acids of the oil was brominated in ether. The insoluble bromo acid was recrystallized and identified as hexabromostearic acid (Table III).

The main portion of the oil was converted to methyl esters by methanolysis and the mixed esters (50 g) were distilled through a spinning band column at 0.5 mm pressure (Table II).

TABLE II
DISTILLATION OF METHYL ESTERS

| Fraction | Temp., °C (0.5 mm) | Weight, g | Chain length | Iodine value | Refractive index, 25° |
|----------|-----------------------|--------------|-----------------|-----------------|--------------------------|
| 1 | 58-63 | 0.48 | | 2.9 | 1.4260 |
| 2 | 63-114 | 1.16 | | 8.0 | 1.4405 |
| 3 | 114-126 | 1.81 | | 75.8 | 1.4490 |
| 4 | 126-136 | 1.57 | | 119.1 | 1.4543 |
| 5 | 136-140 | 13.18 | C_{18} | 126.9 | 1.4558 |
| 6 | 140-147 | 2.04 | | 95.2 | 1.4529 |
| 7 | 147-152 | 1.31 | | 80.9 | 1.4529 |
| 8 | 152-156 | 1.36 | | 79.2 | 1.4529 |
| 9 | 156 | 8.45 | C_{20} | 73.5 | 1.4524 |
| 10 | 156-159 | 13.08 | C_{20} | 57.1 | Solid |
| R | Residue | 4.50 | | | |

Fraction 2 was mainly palmitic ester. Fraction 5 was crystallized from acetone at -25°, giving a little methyl stearate, m.p. 38-38.5°. Oleic and linoleic acids were identified as components of the filtrate by hydroxylation with alkaline permanganate (Table III). Fraction 9 was almost pure methyl eicosenoate but yielded a little methyl arachidate, m.p. 45-45.5°. Fraction 10 gave arachidic acid in quantity. The identity of these acids was confirmed by mixed melting point in each case.

TABLE III
IDENTIFICATION OF ACIDS

| Fraction | Acid | Identified as: | Melting point, °C |
|----------|---------------|-----------------------------------------------------|-------------------|
| 2 | Palmitic | Palmitic acid | 62-62.5 |
| — | Linolenic | Hexabromostearic acid | 180-181 |
| 5 | Linoleic | erythro,erythro-9,10,12,13-Tetrahydroxystearic acid | 171-172 |
| 5 | Oleic | erythro-9,10-Dihydroxystearic acid | 129-130 |
| 5 | Stearic | Methyl stearate | 38-38.5 |
| 9 | 11-Eicosenoic | erythro-11,12-Dihydroxyeicosanoic acid | 129-130 |
| | | 11-Eicosenoic N-hydroxyamide | 69-70 |
| 10 | Arachidic | Arachidic acid | 74.5-75 |

Examination of the residue gave evidence of saturated and monounsaturated acids of chain length C_{22} (equivalent weights 343 and 342). Several of the intermediate fractions were examined further by gas chromatography.

Estimation of the fatty acid composition from all of the data gives the percentages shown in Table IV. The undetermined portion includes a low-molecular-weight acid and C_{22} acids.

TABLE IV
ESTIMATED FATTY ACID COMPOSITION (% OF TOTAL FATTY ACIDS)

| Acid | % | Acid | % |
|-----------|----|---------------|----|
| Palmitic | 3 | Stearic | 2 |
| Linolenic | 8 | 11-Eicosenoic | 42 |
| Linoleic | 8 | Arachidic | 10 |
| Oleic | 22 | Undetermined | 5 |

DISCUSSION

The oil is unique in having eicosenoic acid as the chief component acid in its glycerides. The amount, 42% of the total fatty acids, is double that of the oils previously known to have a high eicosenoic acid content (18-20%) (1, 2).

As a source of this acid, the seed would compare favorably with jojoba seed (*Simmondsia californica* Nuttall), which contains a liquid wax having eicosenoic as its major fatty acid. The content of total fatty acids in jojoba wax is 50% (4) as compared to about 90% in *Cardiospermum* oil. The eicosenoic acid from all of the seed oils and jojoba wax has been identified as the Δ^{11} -isomer.

Isolation of 11-eicosenoic acid from *Cardiospermum* oil tends to confirm previous indications of a C_{20} unsaturated acid in the Sapindaceae family, viz., in species of *Nephelium* (5), *Dodonea* (6), and *Schleichera* (7). The amounts reported were 4.2, 3.1, and 8.9% of the fatty acids respectively, but the acid was not identified further in these instances. The present work shows that the family includes at least one species in which 11-eicosenoic acid is a major component of the seed oil.

The fatty acids of *C. halicacabum* include also arachidic, linolenic, and a low-molecular-weight acid, as found by Covello (3) and confirmed here.* Arachidic acid is in rather large amount (10%), and the quantity of palmitic acid is correspondingly small. This is

*Covello made a careful identification of linolenic acid by converting it to hexabromo- and hexahydroxystearic acids. However, he did not report identification of linoleic acid. His later mention of linoleic acid (ref. 3, p. 783) is manifestly a typographical error and should read "linolenic acid".

characteristic of Sapindaceae oils. There is an appreciable content of linolenic acid. Its presence and amount, about 8%, are unusual for an oil of iodine value below 100.

REFERENCES

1. CHISHOLM, M. J. and HOPKINS, C. Y. *Can. J. Chem.* **31**, 1131 (1953).
2. CHISHOLM, M. J. and HOPKINS, C. Y. *Can. J. Chem.* **34**, 459 (1956).
3. COVELLO, M. *Ann. chim. (Rome)*, **41**, 780 (1951).
4. ECKEY, E. W. and MILLER, L. P. *Vegetable fats and oils*. Reinhold Publishing Corp., New York. 1954. p. 613.
5. HILDITCH, T. P. and STAINSBY, W. J. *J. Soc. Chem. Ind.* **53**, 197T (1934).
6. KOCHAR, R. K. and DUTT, S. *Indian Soap J.* **14**, 132 (1948).
7. WEERAKOON, A. H. Thesis, University of Liverpool. 1952.

GUANIDINE COMPOUNDS

II. PREPARATION OF MONO- AND N,N-DI-ALKYLGUANIDINES^{1,2}

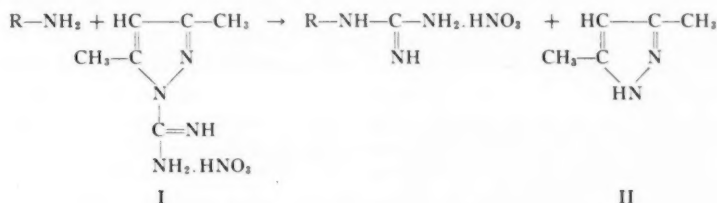
R. A. B. BANNARD, A. A. CASSELMAN, W. F. COCKBURN, AND G. M. BROWN

ABSTRACT

1-Guanyl-3,5-dimethylpyrazole nitrate is superior to S-methylisothiuronium sulphate as a reagent for preparation of simple salts of mono- and N,N-di-alkylguanidines from cyclohexylamine, *trans*-2-aminocyclohexanol, pyrrolidine, and piperidine. S-Methylisothiuronium sulphate, however, gave a higher conversion in the case of dimethylamine. Cyanamide is not as useful a guanylation agent as those mentioned above. The paper chromatography of the mono- and N,N-di-alkylguanidines and the parent amines was studied using four solvent systems.

INTRODUCTION

Of the numerous methods reported in the literature for preparation of mono- and N,N-di-alkylguanidines, those which have been used most frequently are the Erlenmeyer synthesis (1), from amine salts and cyanamide (2, 3, 4, 5, 6), and the Rathke synthesis (7), from amines and an alkylisothiuronium or alkylisouronium salt (8, 9, 10, 11, 12). Both methods, however, frequently lead to poor yields of alkylguanidines, due principally to the formation of dicyandiamide by dimerization of cyanamide on the one hand (13) or hydrolysis of the alkylisouronium salt on the other (8, 14). In 1953, Scott, O'Donovan, and Reilly (15) described the preparation of a number of guanidine picrates in high yield by reaction of amines with 1-guanyl-3,5-dimethylpyrazole nitrate (I) as shown below.



The sole by-product was 3,5-dimethylpyrazole (II) and the method thus seemed a suitable candidate to replace the older methods of synthesis, provided that salts other than the picrates used (15) to simplify recovery of the alkylguanidines proved isolable in high yields. Since we required a number of alkylguanidines in connection with other studies, it seemed of interest to evaluate the usefulness of the three methods of synthesis.

RESULTS AND DISCUSSION

Several procedures for guanylation of amine salts with cyanamide in aqueous or alcoholic solution (2, 4, 5, 6) were examined but all of these in our hands gave yields of alkylguanidines in the range 0-20%. The only method found to be effective was a fusion technique due to Sugino *et al.* (16, 17), by which procedure cyclohexylguanidine hydrochloride was obtained in 48% yield. Guanylation of *trans*-2-aminocyclohexanol

¹Manuscript received July 23, 1958.

Contribution from Defence Research Chemical Laboratories, Ottawa, Canada.

Issued as D.R.C.L. Report No. 284.

²For Part I see ref. 27.

hydrochloride in the same manner, however, gave an intractable mixture and the method was not studied further when it became evident that the other two processes under examination are more reliable.

For guanylation of amines with S-methylisothiuronium sulphate, Phillips and Clarke's procedure (8) was modified by using 1.5 equivalents of amine per equivalent of guanylation agent, this being the ratio of reactants best suited to facile recovery of the alkylguanidine salt in a high state of purity. Results obtained using several primary and secondary aliphatic or heterocyclic amines are given in Table I.

TABLE I
GUANYLATION OF AMINES

| Amine | Product isolated | % Yield | |
|-----------------------------------|-------------------------------------|-----------------------------------|------------------------------------|
| | | Isothiuronium method ^a | Guanylpurazole method ^b |
| Dimethylamine | N,N-Dimethylguanidine | 89.0 ^a | 66.8 ^{c, e} |
| Piperidine | 1-Guanylpiperidine | 65.4 ^a | 80.5 ^{c, f} |
| Pyrrolidine | 1-Guanylpyrrolidine | 59.0 ^a | 80.0 ^{c, f} |
| Cyclohexylamine | Cyclohexylguanidine | 54.5 ^b | 84.8 ^{c, f} |
| <i>trans</i> -2-Aminocyclohexanol | <i>trans</i> -2-Guanidocyclohexanol | 47.6 ^a | 75.8 ^{d, g} |

^aSolvent—aqueous amine, 1.5 equivalents of amine per equivalent of isothiuronium salt.

^b10 mole amine per mole guanylpurazole salt.

^cSolvent—amine.

^dSolvent—ethanol.

^eIsolated as sulphate.

^fIsolated as hydrochloride.

^gIsolated as nitrate.

In the case of pyrrolidine, cyclohexylamine and *trans*-2-aminocyclohexanol separation of the guanidine sulphates from the amine sulphates formed as by-products proved troublesome. However, 1-guanylpiperidine and cyclohexylguanidine were readily isolated as the nitrate and hydrochloride respectively after treatment of the crude product with a strong anion exchange resin. This simple expedient did not succeed for purification of *trans*-2-guanidocyclohexanol sulphate, but for this purpose three methods proved satisfactory. A three-column ion exchange process gave a 70% recovery of *trans*-2-guanidocyclohexanol sulphate. Paper chromatography on seed-test paper (18) gave a 78% recovery but was not suitable on a preparative scale. In the most satisfactory method, the large difference in water solubility of the picrates was utilized, and after purification, *trans*-2-guanidocyclohexanol picrate was converted to the sulphate by ion exchange with an over-all recovery of 66%. It is of interest to note in this connection that Angyal and Warburton (19) were unable to convert picrates of alkylguanidines to simple salts. This observation explains our reluctance to estimate yields in guanylation reactions by conversion to the readily isolable picrates as other workers have done (15) because we wished to obtain simple salts. The use of a strong anion exchange resin, however, now apparently assures reconversion of alkylguanidine picrates to simple salts in high yields.

For guanylation with 1-guanyl-3,5-dimethylpyrazole nitrate, procedures used by Scott, O'Donovan, and Reilly (15) were followed, but in all cases the alkylguanidines were isolated as simple salts rather than picrates. The results given in Table I make it evident that the guanylpurazole method is clearly superior to the isothiuronium method except for preparation of N,N-dimethylguanidine sulphate. It seemed desirable to determine whether the large excess of amine employed by Scott *et al.* (15) could be

reduced to a more reasonable level without seriously impairing the yield of alkylguanidine. Accordingly, several modifications in procedure were used in guanylation of *trans*-2-aminocyclohexanol. Using ethanol as solvent, an intractable mixture resulted when equimolar quantities of reactants were used but a twofold excess of amine led to a 65% yield of *trans*-2-guanidocyclohexanol. The same substance was obtained in 56% yield when an intimate mixture of equimolar quantities of reactants was fused for 1 hour at 100°. The latter modification should prove of value for guanylation of difficultly accessible amines.

The possibility of using the Sakaguchi (20) alkaline hypochlorite - α -naphthol reaction or the Fearon (21) alkaline hypochlorite - thymol reaction to follow the appearance of guanido compounds in reaction mixtures has been examined. The Sakaguchi reaction, which is specific for monosubstituted guanidines (22), has been used for quantitative estimation of certain compounds and optimum conditions for these methods are quoted in the literature. However, these procedures are too time consuming and rapid qualitative methods for the Sakaguchi and Fearon tests are described in the experimental section. S-Methylisothiuronium sulphate, cyanamide, and dicyandiamide interfere with the color reactions and the tests are thus unsatisfactory for following the appearance of guanido compounds in reaction mixtures containing such contaminants. The Sakaguchi test is more satisfactory than the Fearon test, since the latter is both less sensitive and more subject to interference.

The paper chromatographic behavior of the mono- and N,N-di-alkylguanidines was studied in four solvent systems in relation to the behavior of the parent amines (or salts) and certain other substances containing a guanido group. The results summarized in Table II make it clear that for separation of alkylguanidines from the corresponding amines the two solvent systems containing *n*-butanol are superior but that for separation of the guanido acids the two systems containing *tert*-butanol are preferable.

TABLE II
R_F VALUES OF AMINES AND ALKYLGUANIDINES

| Compound | <i>R_F</i> in solvent system* | | | |
|-------------------------------------------------|-----------------------------------------|------|------|------|
| | 1 | 2 | 3 | 4 |
| N,N-Dimethylguanidine sulphate | 0.22 ^{a, b} | 0.19 | 0.70 | 0.44 |
| Dimethylamine hydrochloride | 0.36 | 0.12 | 0.69 | 0.36 |
| 1-Guanylpiperidine nitrate | 0.57 | 0.42 | 0.73 | 0.56 |
| Pyrrolidine | 0.51 | 0.21 | 0.74 | 0.48 |
| 1-Guanylpiperidine hydrochloride | 0.65 | 0.44 | 0.76 | 0.70 |
| Piperidine | 0.59 | 0.27 | 0.77 | 0.55 |
| <i>trans</i> -2-Guanidocyclohexanol nitrate | 0.68 ^c | 0.47 | 0.78 | 0.72 |
| <i>trans</i> -2-Aminocyclohexanol hydrochloride | 0.55 | 0.35 | 0.73 | 0.60 |
| Cyclohexylguanidine hydrochloride | 0.80 | 0.60 | 0.83 | 0.84 |
| Cyclohexylamine hydrochloride | 0.73 | 0.50 | 0.81 | 0.82 |
| L-Canavanine sulphate | 0.05 | 0.02 | 0.09 | 0.16 |
| L-Arginine | 0.19 | 0.03 | 0.46 | 0.19 |
| Guanidoacetic acid | 0.25 | 0.13 | 0.50 | 0.42 |
| α -Guanidopropionic acid | 0.39 | 0.29 | 0.63 | 0.59 |
| β -Guanidopropionic acid | 0.41 | 0.21 | 0.66 | 0.52 |

*1. *n*-Butanol, acetic acid, water (25:6:25 v/v).

2. *n*-Butanol, 1% hydrochloric acid (5:6 v/v).

3. *tert*-Butanol, acetic acid, water (2:1:1 v/v).

4. *tert*-Butanol, 1% hydrochloric acid (3:1 v/v).

^aAll substances except canavanine gave a blue spot with bromcresol green.

^bWeber reagent gave pink or purple spots with the guanidine compounds and a white spot with amines.

^cSakaguchi reagent gave a red or pink spot with monoalkylguanidines and a greenish yellow spot with canavanine.

EXPERIMENTAL^{1,2}*1-Guanyl-3,5-dimethylpyrazole Nitrate*

Aminoguanidine nitrate (68.0 g, 0.500 mole) was added portionwise over a period of 1½ hours to a refluxing solution of 2,4-pentanedione (50.0 g, 0.500 mole) in 50% aqueous ethanol (140 ml) and the resultant solution heated under reflux for 2½ hours. The crystals which separated when the solution was allowed to stand overnight were collected, washed with ether, and dried *in vacuo*. Further crops were obtained by dilution of the filtrate with ether. Recrystallization of the combined crude substances (78.3 g) from ethanol gave 64.6 g (64.6%) of 1-guanyl-3,5-dimethylpyrazole nitrate as colorless prisms, m.p. 166–168°. Thiele and Dralle (23) report m.p. 168°. A small sample was converted to the picrate, which had m.p. 206–208.5° after recrystallization from ethanol (cf. Scott and Reilly (24)).

Aminoguanidine Nitrate

Aminoguanidine bicarbonate was converted to the nitrate salt and the crude product recrystallized from ethanol-ether. Yield, 94% m.p. 142–144°. Theile (25) reports m.p. 144°.

Cyanamide

Cyanamide obtained from the Eastman Kodak Co. was treated with anhydrous ether. The insoluble dicyandiamide was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*, yielding colorless hygroscopic cyanamide, m.p. 40–41° (26).

Cyclohexylguanidine Hydrochloride

(a) *Guanylpurazole method*.—1-Guanyl-3,5-dimethylpyrazole nitrate (2.01 g, 0.01 mole) and cyclohexylamine (9.92 g, 0.100 mole) were heated under reflux with mechanical stirring for 2½ hours in a carbon-dioxide-free apparatus. The resultant pale yellow solution was evaporated to dryness *in vacuo* and the oily residue triturated with anhydrous ether (8×15 ml) to remove by-product 3,5-dimethylpyrazole. Attempts to crystallize the crude cyclohexylguanidine nitrate proved fruitless and the oily material (2.16 g) was dissolved in water (50 ml) and passed through Amberlite IRA-400 (Cl⁻) resin. The resin was washed with water until the effluent gave a negative Sakaguchi test. The combined effluents were evaporated to dryness *in vacuo* and the colorless crystalline residue was recrystallized from ethanol, yielding 1.51 g (84.8%) of cyclohexylguanidine hydrochloride as stout colorless needles, m.p. 228–229°. Calc. for C₇H₁₆N₃Cl: C, 47.32; H, 9.08; N, 23.65; Cl, 19.96%. Found: C, 47.56; H, 8.85; N, 23.40; Cl, 19.80%.

(b) *Isothiuronium method*.—Cyclohexylamine (14.9 g, 0.150 mole), S-methylisothiuronium sulphate (13.9 g, 0.050 mole), and water (40 ml) were mixed at 25° in a carbon-dioxide-free apparatus. On warming the mixture to 40°, brisk evolution of methyl mercaptan began and continued while the temperature was raised to 95° over a period of 3 hours and the isothiuronium salt dissolved. The colorless solution was heated under reflux for 2½ hours, then evaporated to dryness *in vacuo*, yielding 19.0 g of colorless crystalline material. Since earlier preparations had demonstrated the difficulty of separating the cyclohexylguanidine sulphate from by-product cyclohexylamine sulphate, the crude product was converted to the corresponding mixed hydrochlorides via Amberlite IRA-400 (Cl⁻) resin. The eluate from the ion-exchange process was

¹All melting points are uncorrected.

²Microanalyses by Micro-Tech Laboratories, Skokie, Ill., and G. J. Helie of these Laboratories.

evaporated to dryness *in vacuo* and the crystalline residue recrystallized from ethanol, yielding 9.70 g (54.5%) of cyclohexylguanidine hydrochloride, m.p. 228–229° alone, and in admixture with an authentic sample.

(c) *Cyanamide fusion method*.—Cyanamide (3.15 g, 0.075 mole) and cyclohexylamine hydrochloride (6.80 g, 0.050 mole) were intimately mixed, placed in a round-bottomed flask equipped with a reflux condenser and thermometer, and the reaction vessel immersed in a mechanically stirred oil bath at 100°. The temperature of the bath was raised slowly* to 140°, at which temperature fusion of the mixture occurred, accompanied by evolution of white fumes. The temperature of the bath was held at 140–150° for 1 hour, and on cooling, the product solidified, forming a pale yellow glass. The glass was dissolved in glacial acetic acid (150 ml) and the solution was diluted with acetone to precipitate the product as a colorless solid. The latter was collected and recrystallized from ethanol yielding 4.30 g (48.4%) of stout colorless needles, m.p. 228–229° alone, and in admixture with an authentic specimen.

Cyclohexylamine Sulphate

Cyclohexylamine sulphate was obtained as by-product during preparation of cyclohexylguanidine sulphate (27) by interaction of cyclohexylamine and S-methylisothiuronium sulphate. After recrystallization from 80% aqueous ethanol it was obtained as colorless platelets, m.p. 343–346° (decomp.). Calc. for $C_{12}H_{28}N_2SO_4$: C, 48.62; H, 9.52; N, 9.45%. Found: C, 48.73; H, 9.60; N, 9.26%.

dl-trans-2-Guanidocyclohexanol Nitrate

(a) *Fusion method*.—A mixture of 1-guanyl-3,5-dimethylpyrazole nitrate (2.01 g, 0.010 mole) and *dl-trans*-2-aminocyclohexanol (28) (11.5 g, 0.100 mole) was heated at 100° for 2 hours with frequent agitation and exclusion of carbon dioxide. After cooling, the melt was transferred to a Soxhlet extractor and extracted with anhydrous ether for removal of the by-product 3,5-dimethylpyrazole and unreacted amine. The residue was recrystallized from acetone (25 ml), yielding 1.54 g (70.0%) of *dl-trans*-2-guanidocyclohexanol nitrate as fine colorless platelets, m.p. 137–139°. Calc. for $C_7H_{16}N_4O_4$: C, 38.19; H, 7.32; N, 25.44%. Found: C, 38.11; H, 7.34; N, 25.68%. A 57.5% recovery of the unreacted amine was obtained via isolation of the hydrochloride (28). The experiment was repeated under conditions identical with those described above except that equimolar quantities of reactants were used. Yield, 1.23 g (55.8%).

(b) *In ethanol*.—1-Guanyl-3,5-dimethylpyrazole nitrate (2.01 g, 0.010 mole) and *dl-trans*-2-aminocyclohexanol (11.5 g, 0.100 mole) were dissolved in ethanol (50 ml) and the solution was heated under reflux for 2 hours in a carbon-dioxide-free atmosphere. The solution was evaporated to dryness *in vacuo*, and the residue was purified as described in (a) above, yielding 1.67 g (75.8%) of *dl-trans*-2-guanidocyclohexanol nitrate, m.p. 137–139°. A 75.5% recovery of the unreacted amine was effected via the hydrochloride. The experiment was repeated using a twofold excess of amine under otherwise the conditions specified above. Yield, 1.43 g (65.0%).

dl-trans-2-Guanidocyclohexanol Sulphate

dl-trans-2-Aminocyclohexanol (17.3 g, 0.150 mole), S-methylisothiuronium sulphate (13.9 g, 0.05 mole), and water (45 ml) were caused to react under the same conditions

*If the rate of temperature rise exceeds approximately 1° per minute as the fusion point is reached, the reaction becomes very exothermic, causing the temperature of the melt to rise to approximately 200°.

described for preparation of cyclohexylguanidine hydrochloride. The resultant crude mixture of *dl-trans*-2-guanidocyclohexanol sulphate and *dl-trans*-2-aminocyclohexanol sulphate (21.4 g) was treated with boiling methanol (75 ml) and the insoluble crystalline platelets collected and washed with methanol (2×10 ml). This substance (5.35 g) was identified as *dl-trans*-2-aminocyclohexanol sulphate by paper chromatography. The methanolic filtrate was evaporated to dryness *in vacuo* and the resultant colorless solid triturated with anhydrous ether to remove unreacted *trans*-2-aminocyclohexanol. The insoluble material was recrystallized from methanol, yielding 14.9 g of colorless crystalline substance, m.p. 210–220°, which was shown by paper chromatography to be *dl-trans*-2-guanidocyclohexanol sulphate contaminated with a small amount of the corresponding amine sulphate. Purification via the picrate, followed by reversion to the sulphate (see below), gave 9.80 g (54.4%) of *dl-trans*-2-guanidocyclohexanol sulphate, m.p. 223–224°, as fine colorless needles. Calc. for $C_{14}H_{22}N_6SO_6$: C, 40.76; H, 7.82; N, 20.38; S, 7.77%. Found: C, 40.96; H, 7.91; N, 19.86; S, 7.55%.

dl-trans-2-Guanidocyclohexanol Picrate

dl-trans-2-Guanidocyclohexanol nitrate was converted to the picrate in 74.5% yield, m.p. 163–165°, after recrystallization from water. Solubility, ca. 1.6 g/100 ml water at 4°. Calc. for $C_{13}H_{18}N_6O_8$: C, 40.41; H, 4.70; N, 21.76%. Found: C, 40.76; H, 4.82; N, 21.94%.

dl-trans-2-Aminocyclohexanol Sulphate

dl-trans-2-Aminocyclohexanol (28) was converted to the sulphate in 91.5% yield. After recrystallization from 90% ethanol the substance was obtained as colorless platelets which sintered at 265° but did not melt. Calc. for $C_{12}H_{22}N_2SO_6$: C, 43.88; H, 8.59; N, 8.53; S, 9.76%. Found: C, 44.04; H, 8.74; N, 8.24; S, 9.67%.

dl-trans-2-Aminocyclohexanol Picrate

dl-trans-2-Aminocyclohexanol was converted to the picrate in 73.5% yield, m.p. 153–155°, after recrystallization from water. Solubility ca. 15 g/100 ml water at 4°. Calc. for $C_{12}H_{16}N_4O_8$: C, 41.86; H, 4.68; N, 16.28%. Found: C, 41.96; H, 4.69; N, 16.32%.

Purification of dl-trans-2-Guanidocyclohexanol Sulphate Contaminated with *dl-trans*-2-Aminocyclohexanol Sulphate

(a) *Picrate separation method*.—Crude *dl-trans*-2-guanidocyclohexanol sulphate (2.74 g), m.p. 210–220°, from the isothiuronium process was converted to the picrate, yielding 3.72 g (72.4%) of *dl-trans*-2-guanidocyclohexanol picrate, m.p. 163–165°, alone and in admixture with an authentic specimen. A portion of the picrate (1.93 g, 0.0050 mole) was dissolved in methanol and passed through a column of Amberlite IRA-400 (SO_4^-) resin (20 ml) which had been prepared in the usual manner and solvent-exchanged with methanol. The resin was washed with water until the effluent gave a negative Sakaguchi test. The combined eluates were evaporated to dryness *in vacuo* and the residue was recrystallized from methanol, yielding 0.94 g (91.2%) of *dl-trans*-2-guanidocyclohexanol sulphate, m.p. 222–224° (recovery 66%).

(b) *Ion exchange method*.—An Amberlite IRA-400 (OH^-) resin column (60 ml) was connected in series to an Amberlite IRC-50 (H^+) column (9.5 ml). Crude *dl-trans*-2-guanidocyclohexanol sulphate (5.60 g), m.p. 210–220°, was dissolved in water (130 ml) and the solution passed through the resin columns. Just sufficient guanido compound was used to ensure a slight "breakthrough" of alkylguanidine from the IRC-50 column as revealed by the Sakaguchi test. The IRC-50 column was disconnected, and eluted with

5% hydrochloric acid. The eluate was evaporated to dryness *in vacuo*, the residue dissolved in water (50 ml), and the solution passed through an Amberlite IRA-400 (SO_4^-) column (60 ml). The eluate was evaporated to dryness *in vacuo* and the residue recrystallized from methanol, yielding 3.90 g (69.6%) of *dl-trans*-2-guanidocyclohexanol sulphate, m.p. 222–224°.

(c) *Paper chromatographic method.*—An 18½ in. × 22 in. sheet of Whatman seed-test paper was washed chromatographically with 0.1 *N* hydrochloric acid (3 days), with water (4 days), with *n*-butanol, 1% hydrochloric acid (5:6) (1 day), and finally with water (2 days). Crude *dl-trans*-2-guanidocyclohexanol, m.p. 210–220° (200 mg), was applied in aqueous solution (2%) as a streak on the start-line and the chromatogram was developed for 66 hours by the descending technique in a "Chromatocab" using the above-mentioned solvent system. After drying at 40° reference strips were cut from the chromatogram and sprayed with Sakaguchi reagent. The band of alkylguanidine was marked, cut out, eluted with water (100 ml), and treated with Amberlite IRA-400 (SO_4^-) resin to reconvert to the sulphate. The solution was evaporated to dryness *in vacuo* and the residue was recrystallized from methanol, yielding 157 mg (78%) of *dl-trans*-2-guanidocyclohexanol sulphate, m.p. 223–224°.

1-Guanylpyrrolidine Nitrate

(a) *Guanylpiprazole method.*—1-Guanyl-3,5-dimethylpyrazole nitrate (10.0 g, 0.0497 mole) and pyrrolidine (35.5 g, 0.498 mole) were heated under reflux for 2½ hours in a carbon-dioxide-free atmosphere. The product was isolated as described for the preparation of cyclohexylguanidine hydrochloride, except that 1-guanylpyrrolidine nitrate proved readily crystallizable from ethanol and was obtained as stout colorless prisms, m.p. 157–157.5°. Yield, 7.00 g (80.0%). Calc. for $\text{C}_5\text{H}_{12}\text{N}_4\text{O}_3$: C, 34.09; H, 6.87; N, 31.80%. Found: C, 34.20; H, 6.95; N, 32.10%.

(b) *Isothiuronium method.*—Pyrrolidine (10.7 g, 0.150 mole), S-methylisothiuronium sulphate (13.9 g, 0.05 mole), and water (40 ml) were caused to react under the conditions described for preparation of cyclohexylguanidine hydrochloride. The colorless mixture of 1-guanylpyrrolidine sulphate and pyrrolidine sulphate resulting from the evaporation step was dissolved in water (650 ml), the solution passed through Amberlite IRA-400 (NO_3^-) resin, and the latter washed with water until the effluent gave a negative Weber test (29). The combined eluates were evaporated to dryness *in vacuo* and the colorless residue recrystallized from ethanol, yielding 10.4 g (59.0%) of 1-guanylpyrrolidine nitrate as stout colorless prisms, m.p. 157–157.5° alone and in admixture with an authentic specimen.

1-Guanylpiperidine Hydrochloride

1-Guanyl-3,5-dimethylpyrazole nitrate (2.01 g, 0.010 mole) and piperidine (8.52 g, 0.100 mole) were caused to react under the conditions described for preparation of cyclohexylguanidine hydrochloride and the product was isolated as described in the same preparation, since the nitrate salt of 1-guanylpiperidine did not prove to be readily crystallizable. Recrystallization from ethanol-acetone gave 1.32 g (80.5%) of 1-guanylpiperidine hydrochloride as fine colorless needles, m.p. 187–188.5°. Calc. for $\text{C}_6\text{H}_{14}\text{N}_3\text{Cl}$: C, 44.03; H, 8.62; N, 25.68; Cl, 21.67%. Found: C, 44.22; H, 8.74; N, 25.18; Cl, 21.63%.

1-Guanylpiperidine Sulphate

Piperidine (12.8 g, 0.150 mole), S-methylisothiuronium sulphate (13.9 g, 0.05 mole), and water (40 ml) were caused to react under the conditions specified for preparation of

cyclohexylguanidine hydrochloride. Recrystallization of the crude product from 75% aqueous alcohol gave 11.5 g (65.4%) of 1-guanylpiperidine sulphate, as colorless stout prisms, m.p. 284–287° (decomp.). Calc. for $C_{12}H_{23}N_6SO_4$: C, 40.90; H, 8.01; N, 23.85%. Found: C, 40.80; H, 7.98; N, 24.15%. The mother liquor, on treatment with saturated aqueous picric acid gave 5.4 g of piperidine picrate, m.p. 152–153° alone and in admixture with an authentic sample.

N,N-Dimethylguanidine Sulphate

(a) *Guanylpurazole method*.—1-Guanyl-3,5-dimethylpurazole nitrate (2.01 g, 0.010 mole) and dimethylamine (18 g, 25% aqueous solution, 0.100 mole) were heated under reflux for 8 hours in a carbon-dioxide-free atmosphere, using a dry-ice condenser to prevent loss of dimethylamine. The sticky nitrate resulting from evaporation of the solution *in vacuo* was dissolved in water and converted to the sulphate via IRA-400 (SO_4^{2-}) resin. Recrystallization of the crude sulphate from methanol gave 0.91 g (66.8%) of *N,N*-dimethylguanidine sulphate, as fine colorless crystals, m.p. 272–275°. Calc. for $C_6H_{20}N_6SO_4$: C, 26.46; H, 7.40; N, 30.86; S, 11.77%. Found: C, 26.17; H, 7.38; N, 30.67; S, 11.77%.

(b) *Is thiouronium method*.—To a suspension of S-methylisothiuronium sulphate (62.5 g, 0.225 mole) in water (75 ml) at 25° was added a solution of dimethylamine (122 g, 25% aqueous, 0.675 mole) in one portion. A mildly exothermic reaction occurred during which the isothiuronium salt dissolved, methyl mercaptan was evolved, the temperature rose to 35°, and loss of dimethylamine was prevented by use of a dry-ice condenser. The solution was heated under reflux for 30 minutes, then evaporated to dryness *in vacuo*, and the residue recrystallized from methanol, yielding 56.4 g, (89.0%) of *N,N*-dimethylguanidine sulphate, m.p. 272–275° alone, and in admixture with an authentic sample.

Sakaguchi Test for Monoalkylguanidines

For qualitative testing, the guanido compound in 1 ml of water was treated with the following reagents, in the order named, with thorough shaking between each addition. Sodium hydroxide (10% aqueous), 4 drops; α -naphthol solution (0.1% w/v in 95% ethanol), 6 drops; sodium hypochlorite (0.06 *N*, aqueous), 6 drops. The test is positive when the solution develops a pink, red-orange, or cherry-red color within 1 minute. The minimum quantity of cyclohexylguanidine detectable by the method was 5 γ . If more than 6 drops of α -naphthol or sodium hypochlorite solution are used, a yellow "blank" develops which does not interfere with the test.

Fearon Test for Monoalkylguanidines

The procedure was identical with that described for the Sakaguchi test except that it was necessary to use 12 drops of the thymol indicator (0.1% w/v in 95% ethanol). The test is positive when a golden yellow color develops within 1 minute. Three isomeric thymols were tested for usefulness as detectors. Thymol and *o*-thymol were capable of detecting 50 γ of cyclohexylguanidine hydrochloride but *p*-thymol (30) was capable of detecting only 0.5 mg or more of the same substance.

Inhibition of Sakaguchi and Fearon Tests

Cyanamide, dicyandiamide, and S-methylisothiuronium sulphate interfere with the Sakaguchi and Fearon tests. Cyanamide gives colored "blanks" (purple to Burgundy red) at concentrations greater than 0.3 mg/ml, and below this concentration 0.6 *N* hypochlorite must be used to obtain a positive reaction. S-Methylisothiuronium sulphate and dicyandiamide do not give colored blanks but their presence in concentrations

greater than 0.3 mg/ml necessitates the use of 0.6 N hypochlorite. Solutions containing more than 3 mg/ml of S-methylisothiuronium sulphate will not give a positive test if the concentration of guanido compound is less than 50 γ /ml.

Paper Chromatography of Amines and Guanidine Compounds

For paper chromatography, a 10 λ spot of a 2% aqueous solution of the amine or guanidine compound was applied to unwashed Whatman No. 1 paper. The chromatograms were developed for 18 hours in glass chromatographic tanks by the descending technique, using the solvent systems specified in Table II. The air-dried chromatograms were then sprayed with bromocresol green, Weber (29), or Sakaguchi reagent for detection of the substances.

REFERENCES

1. ERLÉNMEYER, E. *Ann.* **146**, 258 (1868).
2. BRAUN, C. E. *J. Am. Chem. Soc.* **55**, 1280 (1933).
3. KING, H. and TONKIN, I. M. *J. Chem. Soc.* 1063 (1946).
4. ODO, K. *J. Chem. Soc. Japan, Pure Chem. Sect.* **71**, 394 (1950).
5. LAWSON, A. *J. Chem. Soc.* 307 (1956).
6. PADEN, J. H. and McLEAN, A. F. *U. S. Pat. No.* 2,425,341 (1947).
7. RATHKE, B. *Ber.* **14**, 1774 (1881); **17**, 297 (1884).
8. PHILLIPS, R. and CLARKE, H. T. *J. Am. Chem. Soc.* **45**, 1755 (1923).
9. KAPFFHAMMER, J. and MÜLLER, H. *Z. physiol. Chem.* **255**, 1 (1934).
10. BRAND, E. and BRAND, F. C. *Org. Syntheses*, **22**, 59 (1942).
11. KURTZ, A. C. *J. Biol. Chem.* **180**, 1253 (1949).
12. MOURGUE, M. *Bull. soc. chim. France*, 181 (1948).
13. TAYLOR, T. W. J. and BAKER, W. *In* Sidgwick's organic chemistry of nitrogen. Oxford University Press, London, 1937, p. 329.
14. SCHÖBEEL, A. and WAGNER, A. *In* Methoden der organischen Chemie. Edited by E. Müller, Georg. Thieme Verlag, Stuttgart, 1955, p. 14.
15. SCOTT, F. L., O'DONOVAN, D. G., and REILLY, J. *J. Am. Chem. Soc.* **75**, 4053 (1953).
16. SUGINO, K., SJIRAI, K., and AOYAGI, K. *Bull. Chem. Soc. Japan*, **17**, 126 (1942).
17. ODO, K. and SUGINO, K. *J. Chem. Soc. Japan*, **63**, 336 (1942).
18. BROWNELL, H. H., HAMILTON, J. G., and CASSELMAN, A. A. *Anal. Chem.* **29**, 550 (1957).
19. ANGYAL, S. J. and WARBURTON, W. K. *J. Chem. Soc.* 2492 (1951).
20. SAKAGUCHI, S. *J. Biochem. Tokyo*, **5**, 13, 25 (1925).
21. FEARON, W. R. *Sci. Proc. Roy. Dublin Soc.* **22**, 415 (1941).
22. MOLD, J. D., LADINO, J. M., and SCHANTZ, E. J. *J. Am. Chem. Soc.* **75**, 6321 (1953).
23. THIELE, J. and DRALLE, E. *Ann.* **302**, 275 (1898).
24. SCOTT, F. L. and REILLY, J. *J. Am. Chem. Soc.* **74**, 4652 (1952).
25. THIELE, J. *Ann.* **270**, 1 (1892).
26. MIGRICHIAN, V. The chemistry of organic cyanogen compounds. Reinhold Publishing Corp., New York, 1947, p. 15.
27. COCKBURN, W. F. and BANNARD, R. A. B. *Can. J. Chem.* **35**, 1285 (1957).
28. HAWKINS, L. R. and BANNARD, R. A. B. *Can. J. Chem.* **36**, 220 (1958).
29. WEBER, C. J. *J. Biol. Chem.* **78**, 465 (1948).
30. BANNARD, R. A. B. and LEITCH, L. C. *Can. J. Chem.* **34**, 1464 (1956).

THE CHEMISTRY OF THE "AMINOCHROMES"

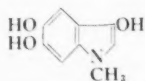
PART II. THE PREPARATION, PAPER CHROMATOGRAPHY, AND SPECTROSCOPIC PROPERTIES OF PURE ADRENOLUTIN; THE INFRARED SPECTRUM OF ADRENOCHROME^{1,2}

R. A. HEACOCK AND (IN PART) M. E. MAHON

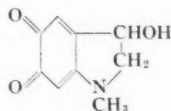
ABSTRACT

The preparation of adrenolutin monohydrate in pure crystalline form has been carried out by the alkaline rearrangement of aqueous solutions of adrenochrome, prepared from the silver oxide oxidation of adrenaline in aqueous solution. An anion-exchange resin (Dowex-1 (Cl⁻)) was employed to remove inorganic contaminants from the reaction mixture prior to treatment with alkali. The pure anhydrous material has been prepared by the high vacuum sublimation of the monohydrate. The paper chromatographic, spectroscopic, and fluorimetric characteristics of adrenolutin have been investigated. On the basis of the infrared spectrum it is suggested that in the solid state, adrenolutin exists in the keto form, i.e. 2,3-dihydro-5,6-dihydroxy-N-methyl-3-ketoindole. The infrared spectrum of adrenochrome, in the solid state, agrees with the zwitterionic formulation suggested for this compound.

Adrenolutin (usually formulated as 3,5,6-trihydroxy-N-methylindole, I), the substance mainly responsible for the intense yellow-green fluorescence that develops in adrenaline solutions that have undergone oxidation in alkaline media, was first isolated in crystalline form and correctly identified by Lund in 1949 (1), from the alkaline rearrangement products of adrenochrome (II), although the correct structure had been assigned to the substance on theoretical grounds a year earlier (Ehrlen (2)).



I



II

The structure was subsequently confirmed by an unambiguous synthesis starting from 3,4-isopropylidenedioxyaniline (Balsiger *et al.* (3)).

The preparation of adrenolutin from adrenaline oxidized with potassium ferricyanide in aqueous bicarbonate buffer, followed by rearrangement with aqueous sodium hydroxide and acidification (4), gave, in our hands, somewhat variable results, and good yields of pure product could not be consistently obtained. It appeared that the product was contaminated with inorganic residues from the oxidation mixture which probably catalyzed its decomposition. It has recently been shown that adrenochrome prepared by the oxidation of adrenaline with silver oxide was often contaminated with traces of silver, and that this contamination could be minimized by passage of the reaction mixture through an ion-exchange resin (Dowex-1 (Cl⁻)) prior to isolation of the products (5). The use of this procedure to remove contaminants from adrenochrome solutions has now been extended to the preparation of adrenolutin, and gave consistently good yields of adrenolutin monohydrate in a pure crystalline form. Although the water of crystallization could be removed by drying in a vacuum desiccator, the anhydrous material was always obtained as an

¹Manuscript received July 21, 1958.

Contribution from the Psychiatric Research Unit, University Hospital, Saskatoon, Saskatchewan. This investigation was supported by grants from the Federal Department of Health and Welfare, and the Rockefeller Foundation. This work was carried out under the auspices of the Saskatchewan Committee on Schizophrenia Research.

²Part I—*Can. J. Chem.* **36**, 853 (1958).

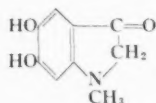
amorphous brownish-green powder. However high vacuum sublimation of the hydrate gave anhydrous adrenolutin in an analytically pure form as a bright yellow crystalline solid.

The paper chromatographic behavior of this substance has already been referred to in Part I of this series (5), and the present investigation has confirmed that the use of acid-washed chromatographic paper is essential when working with adrenolutin, since traces of heavy metals and other impurities present in unwashed papers catalyze the air oxidation of adrenolutin, and on unwashed paper only dark streaks of polymeric oxidation products were observed. The best solvents for paper chromatography appeared to be water ($R_f = 0.45$) or methanol ($R_f = 0.60$). These R_f values were obtained on prewashed Whatman No. 1 paper; a somewhat lower value was observed with water on Whatman No. 54 paper. Acidic solvents caused the characteristic yellow-green fluorescence of the compound to change to a pale pinkish-orange color; alkaline solvents were quite unsuitable and caused its rapid decomposition.

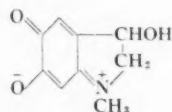
The ultraviolet and visible absorption spectra obtained from samples of adrenolutin prepared as described above corresponded well with those previously published (1). The fluorescence characteristics of this substance are of considerable importance, since they have been utilized for many years in empirical methods for the estimation of adrenaline (cf. Persky (6)). The current investigation has shown that there are slight variations in the maximum wavelengths of excitation and fluorescence depending on the solvent used. The highest intensity of fluorescence emission appeared to occur when acetone was used as solvent, with excitation at $405\text{ m}\mu$ and the fluorescence measured at $490\text{ m}\mu$. In alkaline solution the molecule existed in the phenoxide ion form and in this case the maximum emission was observed at $515\text{ m}\mu$ after excitation at $405\text{ m}\mu$ (cf. 7).

The infrared spectra of anhydrous and hydrated adrenolutin and 3,5,6-triacetoxy-*N*-methylindole ("triacyladrenolutin") were measured in the solid state ("NUJOL" mulls). In the spectrum of the anhydrous compound, the peak at 3360 cm^{-1} was probably due to a hydrogen-bonded hydroxyl group (cf. 8, p. 84). The high-frequency region of the spectrum of the hydrate was more complicated; peaks were observed at 3480 and 2650 cm^{-1} and there were two shoulders on the "NUJOL" (C-H stretching) peak, at 3250 and 3100 cm^{-1} . These bands must presumably have arisen from the hydrogen-bonded phenolic O-H groups and the water of crystallization. It has recently been demonstrated spectroscopically that in the solid state, and in solution in chloroform and carbon disulphide certain indoxyl derivatives exist in the keto form (10). The sharp peak at 1647 cm^{-1} in the spectrum of the anhydrous compound was at a considerably lower frequency than those previously quoted for indoxyl carbonyls, both in chloroform solution and in the solid state (i.e. $1750\text{--}1710\text{ cm}^{-1}$; 9, 10). However, the hydroxy groups at the 5- and 6-positions in the benzene ring would be expected to reduce the carbonyl frequency, e.g. the carbonyl stretching frequency of *p*-hydroxyacetophenone occurs at 1636 cm^{-1} in the solid state ("NUJOL" mull) and at 1653 cm^{-1} in chloroform (concentrated solution), whereas in acetophenone itself the carbonyl frequency occurs at 1686 cm^{-1} (pure liquid) (8, p. 120; 11), and this frequency is further reduced by the presence of a second hydroxy group in the benzene ring (12). Therefore, in the solid state, anhydrous adrenolutin probably exists in the keto form (III) (i.e. 2,3-dihydro-5,6-dihydroxy-*N*-methyl-3-ketoindole). In the case of the hydrate the spectrum in the " $1700\text{--}1600\text{ cm}^{-1}$ " region was somewhat complicated, and the band at 1647 cm^{-1} was not observed, however, there were shoulders at 1632 , 1610 , and 1595 cm^{-1} on a main peak at 1575 cm^{-1} , but in this case no assignment of bands can be made with any degree of certainty. The triacetate exhibited well-defined bands at

1762 and 1740 cm^{-1} , the former being due to the 5,6-diacetoxy groups and the latter to the 3-acetoxy group (cf. Holt *et al.* (10)). Several attempts to measure the infrared



III



IV

spectrum of adrenochrome by the potassium bromide disk technique were unsuccessful, leading only to an ill-defined spectrum without very sharp peaks. It appeared that some decomposition and possibly some isomerization (to adrenolutin) had taken place during the preparation of the disk. However perfectly satisfactory spectra could be obtained from suspensions in "NUJOL". The results obtained can best be interpreted on the grounds of the zwitterionic structure (IV), suggested by Harley-Mason (13). There was an O-H stretching band at 3295 cm^{-1} , and in the "carbonyl region", the main band occurs at 1577 cm^{-1} ; this was probably due to the $\text{C}=\text{O}^-$ group (cf. the strong band of the ionized carboxyl group occurs in this region (8); the bands at 1682, 1672, and 1622 cm^{-1} could be tentatively assigned to the $\text{C}=\text{N}^+$, $\text{C}=\text{O}$ and the conjugated double bonds of the six-membered ring. The spectra of 2-iodoadrenochrome and six other "aminochromes" (14) were essentially the same as that of adrenochrome, indicating that all these compounds exist in the dipolar form.

EXPERIMENTAL

Preparation of Adrenolutin Monohydrate

L-Adrenaline (5.0 g) was suspended in water (150 ml) and concentrated hydrochloric acid added dropwise until a clear solution was obtained. Freshly prepared silver oxide (20.0 g) was added portionwise to the stirred solution and the stirring continued for 2 minutes. The reaction mixture was filtered through a Dowex-1 (Cl^-) (200/400 mesh) resin bed (diam. = 6.5 cm; height = 1.5 cm)* and the filtrate cooled in ice. A stream of nitrogen was passed through the filtrate, cooled in an ice bath, and 10% sodium hydroxide solution (50 ml) added. The brownish-yellow solution, which exhibited a brilliant green fluorescence, was stirred and acidified by the dropwise addition of glacial acetic acid; adrenolutin monohydrate was precipitated as a bright yellow crystalline solid (3.25 g), m.p. 232–235° with decomposition. (Found: C, 54.94; H, 5.56. Calc. for $\text{C}_9\text{H}_{11}\text{O}_4\text{N}$: C, 54.82; H, 5.62.) The product, which was dried at room temperature in a current of nitrogen, could be recrystallized from water (containing a small quantity of sodium hydrosulphite to prevent oxidation) and obtained in bright yellow prisms, m.p. 236° with decomposition.

Preparation of (Anhydrous) Adrenolutin

Adrenolutin monohydrate (0.1 g) was sublimed at 180–200°/3 mm and anhydrous adrenolutin was obtained in bright yellow prisms, m.p. 245° with decomposition. (Found: C, 60.59; H, 4.90. Calc. for $\text{C}_9\text{H}_9\text{O}_3\text{N}$: C, 60.33; H, 5.06.) Neither of these products showed any tendency to decolorize if stored at room temperature in the dry state.

*The resin was prepared by extensive washing with (1) 3 N hydrochloric acid and (2) water until neutral to litmus.

Harley-Mason quotes melting points of 230–232° and 285°* for the monohydrate and anhydrous material respectively (4, 15). Lund states that the substance he isolated decomposes above 100° without melting (1); Balsiger *et al.*, quote melting point 195°* (anhydrous substance) (3), whilst Fischer obtained a melting point of 230–235° for the hydrate (16).

Paper Chromatography of Adrenolutin

Either Whatman No. 1 paper (washed with 2% acetic acid for 12 hours and dried prior to use) or Whatman No. 54 paper was used. Both the ascending and descending techniques were employed, each method gave approximately the same R_f values; *ca.* 20 to 30 μ g of sample were applied to the paper in each case. The solvent was allowed to run a distance of *ca.* 35 cm. The solvents employed, namely water, 2% acetic acid, and methanol all ran very quickly and 2.5 to 3.5 hours were usually required for each run. The results obtained are given in Table I. Since adrenolutin is bright yellow in color its position on the developed chromatogram was usually self-indicating, however, the position of the spot could be confirmed as follows: (a) it showed a characteristic intense yellow-green fluorescence in ultraviolet light; (b) it gave a blue color with the ferric chloride – potassium ferricyanide reagent (*cf.* 5); (c) a violet color slowly developed after spraying with Ehrlich's reagent; (d) Gibb's reagent (*N*-2,6-trichloro-*p*-quinoneimine) gave a brown spot.

TABLE I
PAPER CHROMATOGRAPHIC CHARACTERISTICS OF ADRENOLUTIN

| Solvent system | Water | 2% Acetic acid in water* | Methanol |
|-----------------------------------|-----------------|-----------------------------|-----------------|
| R_f of adrenolutin on: | | | |
| (a) Prewashed Whatman No. 1 paper | 0.45 \pm 0.03 | 0.48 \pm 0.02 | 0.60 \pm 0.01 |
| (b) Whatman No. 54 paper | 0.35 \pm 0.01 | 0.43 \pm 0.03 | 0.60 \pm 0.02 |

*In acidic solvents the adrenolutin spot exhibited a pinkish-orange fluorescence.

Spectroscopic Studies on Adrenolutin, Adrenochrome, and Some Related Compounds

(a) The ultraviolet and visible absorption spectra of adrenolutin were measured on freshly prepared aqueous solutions (10 μ g/ml) using a Beckman DU spectrometer (λ_{\max} : 255, 285, 410 $m\mu$; λ_{\min} : 239, 272, 340 $m\mu$).

(b) The spectrophotofluorimetric characteristics of adrenolutin were determined on a Farrand Spectrophotofluorimeter. Solutions of the anhydrous substance (10 μ g/ml) in the various solvents were prepared immediately before use and the combination of wavelengths of excitation and emission giving the maximum intensity of fluorescence recorded. The results obtained are given in Table II. (The measurements were always

TABLE II
FLUORESCENCE CHARACTERISTICS OF ADRENOLUTIN SOLUTIONS¹ IN VARIOUS SOLVENTS

| Solvent | Excitation maximum (wavelength, $m\mu$) | Fluorescence maximum (wavelength, $m\mu$) | Intensity of fluorescence (arbitrary units) |
|----------------------------------------|---------------------------------------------------|-----------------------------------------------------|------------------------------------------------------|
| Methanol | 405 | 490 | 2000 |
| Distilled water | 410 | 505 | 1400 |
| 0.01 <i>N</i> Aqueous sodium hydroxide | 405 | 515 | 2400 |
| 0.01 <i>N</i> Aqueous acetic acid | 405 | 500 | 1000 |
| Acetone | 405 | 490 | 3400 |

¹Concentration of 10 μ g/ml.

* = with decomposition.

made on freshly prepared solutions owing to the ease with which they undergo oxidative decomposition.)

(c) *The infrared spectra of:* anhydrous adrenolutin, adrenolutin monohydrate, 3,5,6-triacetoxy-*N*-methylindole (14), adrenochrome (5), and 2-iodoadrenochrome (17) were measured as "NUJOL" mulls on a Perkin-Elmer model 21 infrared spectrophotometer using a sodium chloride prism. The first two compounds were prepared as described above and the others were obtained by the methods described in the literature. The main absorption bands observed in three spectral regions are given in Table III.

TABLE III
MAIN ABSORPTION PEAKS IN SPECTRAL REGION INDICATED (IN CM^{-1})

| Compound | A | B | C |
|------------------------------------------|----------------------------------------------------------|-----------------------------------------------------------------------------------------|-------------------------------|
| Anhydrous adrenolutin | 3360 (m) 3100 (m) | 1647 (s) 1600 (m, sh) 1570 (s) 1545-1530 (s) | 880 (m) 855 (w) 820 (w) |
| Adrenolutin monohydrate | 3480 (m) 3250 (m, sh) 3100 (m, sh) 2650 (m, sh) | 1632 (m/s, sh) 1610 (s, sh) 1595 (s, sh) 1575 (s) 1535-1525 (s) 1508 (s) | 855 (m) 825 (m) |
| 3,5,6-Triacetoxy- <i>N</i> -methylindole | — | 1762 (s) 1740 (s) 1632 (w) 1547 (w) | 870 (m) 854 (w) 812 (m) |
| Adrenochrome | 3295 (m) | 1682 (m/s) 1672 (m, sh) 1622 (m) 1575 (s) | 900 (w) 817 (m) |
| 2-Iodoadrenochrome | 3420 (m) | 1674 (m/s) 1657 (w, sh) 1612 (m) 1562 (s) | 871 (m) |

A = 4000-2500 cm^{-1} ; B = 1800-1500 cm^{-1} ; C = 900-800 cm^{-1} .

(s) = strong; (m) = medium; (w) = weak; (sh) = shoulder.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Dr. A. N. Payza of this department for some useful discussion, and to Dr. R. N. Jones and Mr. R. Lauzon of the National Research Council (Ottawa) for assistance in obtaining the infrared spectrum of adrenochrome, and for some helpful suggestions on its interpretation.

REFERENCES

1. LUND, A. *Acta Pharmacol. Toxicol.* **5**, 75, 121 (1949).
2. EHRLÉN, I. *Farm. Revy.* **47**, 242 (1948).
3. BALSIGER, R. W., FISCHER, R. W., HIRT, R., and GIOVANNINI, E. *Helv. Chim. Acta*, **36**, 708 (1953).
4. BU'LOCK, J. and HARLEY-MASON, J. *J. Chem. Soc.* **712** (1951).
5. HEACOCK, R. A., NERENBERG, C., and PAYZA, A. N. *Can. J. Chem.* **36**, 853 (1958).
6. PERSKY, H. *Methods of Biochem. Anal.* **2**, 57 (1955).
7. COHEN, G. and GOLDENBERG, M. *J. Neurochem.* **2**, 58 (1957).
8. BELLAMY, L. J. *The infrared spectra of complex molecules.* Methuen & Co. Ltd., London, 1954.
9. WITKOP, B. and PATRICK, J. B. *J. Am. Chem. Soc.* **73**, 713 (1951).
10. HOLT, S. J., KELLIE, A. E., O'SULLIVAN, D. G., and SADLER, P. W. *J. Chem. Soc.* **1217** (1958).
11. SOLOWAY, A. H. and FRIESS, S. L. *J. Am. Chem. Soc.* **73**, 5000 (1951).
12. SCROCCO, M. and LIBERTI, A. *Ricerca sci.* **24**, 1687 (1954).
13. HARLEY-MASON, J. *Experientia*, **4**, 307 (1948).
14. HEACOCK, R. A. Unpublished observations.
15. HARLEY-MASON, J. *J. Chem. Soc.* **1276** (1950).
16. FISCHER, P. *Bull. soc. chim. Belges*, **58**, 205 (1949).
17. SOBOTKA, H. and AUSTIN, J. *J. Am. Chem. Soc.* **73**, 3077 (1951).

THE ELECTRICAL POLARIZATIONS OF BIS-MERCURIALS¹

HENRY SAWATZKY AND GEORGE F WRIGHT

ABSTRACT

Very dilute solutions of diphenylmercury in carbon tetrachloride have been found not to have orientation polarization, but in not-so-dilute carbon tetrachloride or in dioxane and benzene at any concentration there is evidence of moment. Moreover, these moments vary negatively in carbon tetrachloride and dioxane and positively in benzene with respect to temperature. The angular C-Hg-C linkage responsible for orientation polarization is also demonstrated by appreciable moments for para methylmercuri-*bis*-benzene and the homologous duren. Magnitudes comparable with the aryl analogues are found for several alkyl *bis*-mercurials, but the similarity in the moments of trifluoromethyl and methyl-*bis*-mercury as well as a temperature coefficient for moment of the latter compound indicates that the C-Hg-C linkage may vary widely and easily. However, a lower limit may be set by the moments of mercuracyclohexane and mercuracycloheptane in which the mercury angle is fixed by the cyclic structure.

INTRODUCTION

For several decades the electrical polarization of diphenylmercury has seemed to be anomalous. Originally Bergmann and Schütz found the solute polarization in benzene to be 64 cc at 14.15° and concluded that it was due entirely to electronic polarization (1). Later Hampson (2) found the polarization to be 68.8 cc at 25° in benzene. Since this value exceeded the electronic polarization, and since greater deviations from electronic polarization were found for a number of *p*-disubstituted analogues of diphenylmercury, Hampson concluded that the C-Hg-C bond was angular in these substances. Others, and most recently Armstrong, LeFevre, and LeFevre (3), consider that the data may be better interpreted in terms of abnormal atom polarization. However, a direct measurement (4) has shown that diphenylmercury has a distortion polarization which actually

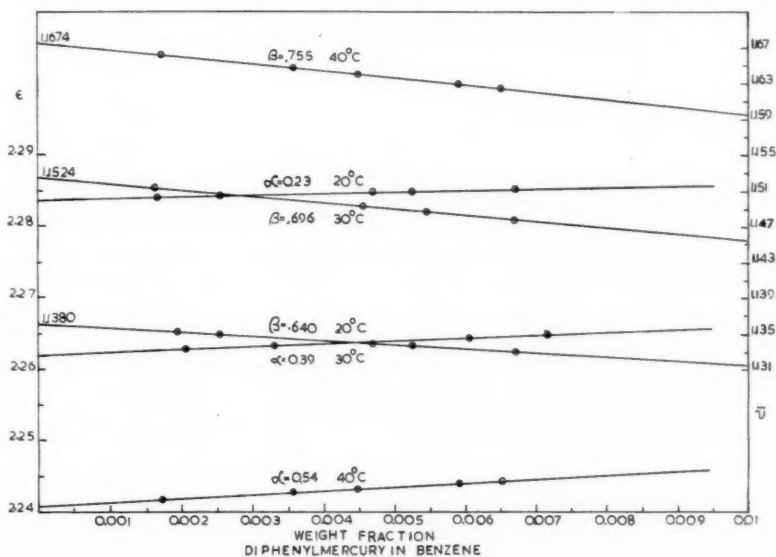


FIG. 1.

¹Manuscript received May 1, 1958.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

is lower than that calculated from refractometric data. In view of this anomalous situation we have now examined a wider variety of *bis*-mercurials and of conditions under which the polarization is determined.

Diphenylmercury

The variation of electric polarization with respect to solvent, concentration, and temperature is shown in Table I. It may be seen in Fig. 1 that in benzene the relationship of both specific volume and dielectric constant is linear with respect to weight fraction even at concentrations less than 0.002, and extrapolation conforms closely with the values for the pure solvent. This seemingly normal behavior is belied by the augmentation of apparent moment as the temperature is increased from 20° to 40° (Table I). By contrast the apparent moment in dioxane (in which equally good linearity and extrapolation of $\delta\epsilon/\delta\omega$ and $\delta\bar{V}/\delta\omega$ have been observed) has shown a diminution as the temperature has been increased. Likewise with weight fractions (ω) of 0.005 to 0.01 it may be seen (Fig. 2) that the apparent moment in carbon tetrachloride decreases as the temperature rises from 20° to 40°. These variations have been plotted in Fig. 3. It is of interest that these curves (which might be straight lines within the ± 0.01 D precision) intersect at about 25°.

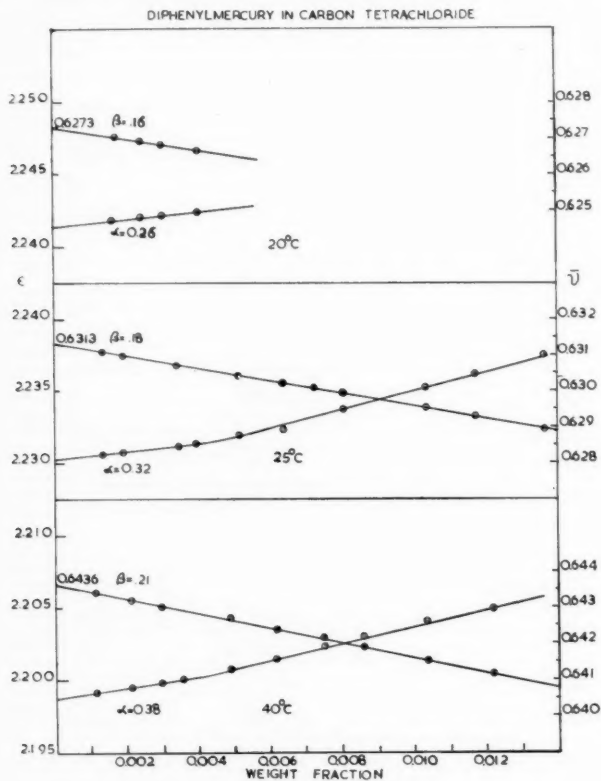


FIG. 2.

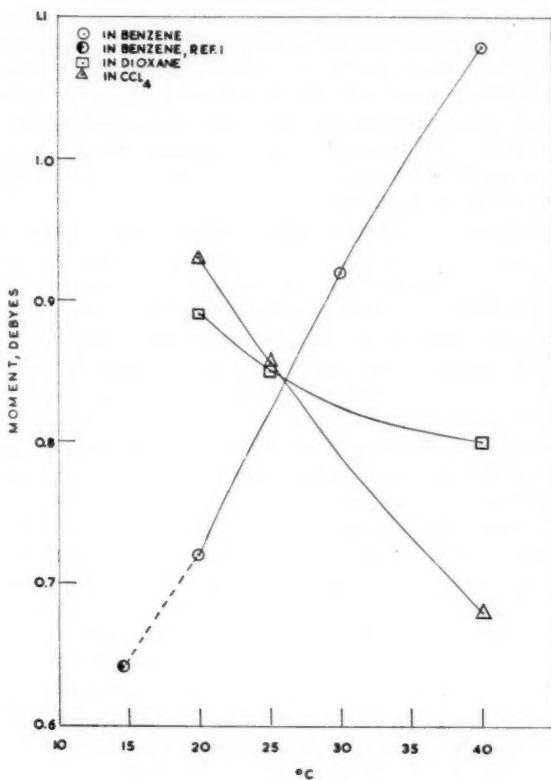


FIG. 3.

TABLE I
DIPOLE MOMENT DATA FOR DIPHENYLMERCURY

| Temp., °C | Wt. fraction range | Solvent | α | β | P_{200}^* cc | μ, D^* |
|-----------|--------------------|------------------|----------|---------|-------------------|------------|
| 40 | 0-0.01 | Benzene | 0.54 | 0.755 | 80.1 | 1.08 |
| 30 | 0-0.015 | Benzene | 0.39 | 0.696 | 74.3 | 0.92 |
| 20 | 0-0.01 | Benzene | 0.23 | 0.640 | 68.2 | 0.72 |
| 40 | 0-0.015 | Dioxane | 0.40 | 0.536 | 69.8 | 0.80 |
| 25 | 0-0.010 | Dioxane | 0.43 | 0.572 | 72.2† | 0.85 |
| 20 | 0-0.015 | Dioxane | 0.46 | 0.507 | 73.9 | 0.89 |
| 40 | 0-0.005 | CCl ₄ | 0.38 | 0.21 | 58.7 | — |
| 25 | 0-0.005 | CCl ₄ | 0.32 | 0.18 | 58.4 | — |
| 20 | 0-0.005 | CCl ₄ | 0.26 | 0.16 | 58.2 | — |
| 40 | 0.005-0.01 | CCl ₄ | 0.58 | 0.212 | 66.3 | 0.68 |
| 25 | 0.005-0.01 | CCl ₄ | 0.67 | 0.174 | 72.2 | 0.85 |
| 20 | 0.005-0.01 | CCl ₄ | 0.73 | 0.163 | 75.2 | 0.93 |

*The P_{200} of 57.1 as obtained from solid dielectric data is used for the calculations of the dipole moments.

†Contrasted to Curran's 69.02 (6).

The observed polarization at 25° in carbon tetrachloride (71.6 cc) is not far from that reported (70.2 cc) by Armstrong, LeFevre, and LeFevre (3). However, it may also be seen in Fig. 2 that the latter agreement was attained only by using the concentration range specified by the three authors (3). In the concentration range of 0–0.005 weight fraction it is apparent that a sharply different $\delta\epsilon/\delta\omega$ (α) prevails at all temperatures, although no such inflection is observed in the $\delta\bar{V}/\delta\omega$ slope. The latter evidence for the constancy of β is confirmed by isopiestic measurements which show that diphenylmercury does not associate in carbon tetrachloride.

There have been doubts (3) about the significance of the value for distortion polarization (57.1 cc) determined from the dielectric constants of solid diphenylmercury pellets. The critics considered this value to be low, but the criticism is not entirely justified in view of the total polarizations (in cc, 58.2, 58.6, and 58.7) found at 20, 30, and 40° for diphenylmercury in very dilute tetrachloride solution. An assignment of orientation polarization which exceeds these values must be erroneous. Although our measured distortion polarization (57.1 cc) is 1.1 to 1.6 cc below the total polarizations mentioned above, we cannot safely assign the differences to orientation polarization. These differences are only slightly outside our experimental error. We cannot say whether the moment of diphenylmercury in dilute carbon tetrachloride solution is zero or whether it has a very low value which cannot be defined by the present experimental techniques. But we can say that the minimal polarizations which we have observed in very dilute carbon tetrachloride solutions are contradictory rather than confirmatory to recent claims (3) of zero dipole moment for diphenylmercury, because we have set a minimum which the distortion polarization cannot exceed.

In order to arrive at these conclusions it has been necessary to give careful attention to the purity of the carbon tetrachloride. For example the use of an old sample ($\epsilon_0 = 2.2303$ and $\bar{V} = 0.6312$) for the polarization study of diphenylmercury shows a decrease in $\delta\epsilon/\delta\omega$ at 25° (in the concentration range $\omega = 0.005$ to 0.01) from 0.67 (in the pure solvent where $\epsilon_0 = 2.2268$) to 0.50 in the old solvent, although the change in $\delta\bar{V}/\delta\omega$ does not exceed 0.01. Of course, this behavior is not unprecedented (p. 130, ref. 5) when the polarity of the solvent is increased. While we have been unable to characterize the impurity which raised the dielectric constant of the old carbon tetrachloride, we have found that deliberate addition of water to our purest solvent (resultant $\epsilon_0 = 2.2289$ at 25°) lowers $\delta\epsilon/\delta\omega$ from 0.67 to 0.48, while $\delta\bar{V}/\delta\omega$ decreases from 0.174 to 0.163. Since these differences lower the apparent moment from 0.85 D to 0.63 D it is evident that rigorously purified solvent must be used for meaningful results.

The variation in polarization with respect to concentration may indeed provide an insight into the molecular behavior of diphenylmercury, especially since the medium, carbon tetrachloride, in which this variation occurs is tetrahedrally symmetrical, with little tendency toward co-ordination. We suggest that in this medium diphenylmercury is self-polarized at the higher concentrations. We presume that the effect of this self-polarization is a reduction in the tendency for diphenylmercury molecules to execute the 360° rotation which is ineffective toward the external field. We believe that this rotation, a consequence of the mass of the central atom, is indicated by the evident perturbation in the spectral absorption at 463 cm⁻¹.

It follows that in very dilute solution more molecules, freed from self-polarization, will completely rotate. The same circumstance ought to reduce the polarization at increased temperatures. This effect is observed (Fig. 3) in carbon tetrachloride.

In this connection it is of interest to compare the dielectric constants of pure carbon

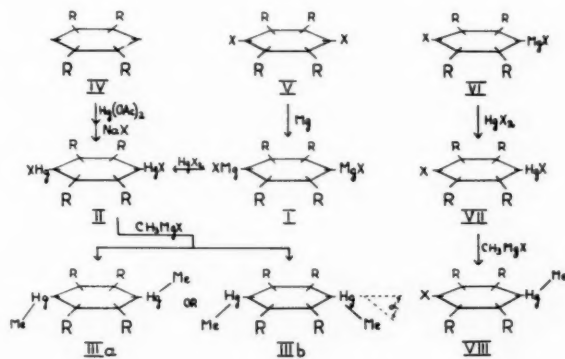
tetrachloride at the several temperatures with the extrapolation to zero solute concentration. It is evident that the extrapolations for very dilute solutions must differ from those for not-so-dilute solutions. The extrapolation of $\delta\epsilon/\delta\omega$ for very dilute solutions is essentially indistinguishable from that of the pure solvent; ϵ_0 (solvent) minus ϵ_0 (solution) is less than 0.0002. On the other hand the extrapolation of $\delta\epsilon/\delta\omega$ for not-so-dilute solution shows at 20° C that ϵ_0 (solvent) minus ϵ_0 (solution) is 0.001, but at 40° it has decreased to 0.0005. This behavior would indicate that the solvent cavities differ in the two concentration ranges, and suggests that the effectively larger cavity due to self-polarization is decreased either by separation of diphenylmercury molecules, or by thermal agitation.

Benzene is not tetrahedrally symmetrical, so interaction of diphenylmercury with this medium is not unexpected. This interaction ought to minimize self-polarization and it should prevail over the entire concentration range. This expectation is realized in the linearity of the $\delta\epsilon/\delta\omega$ graph over a weight fraction range of 0.001 to 0.008 (Fig. 1) and more.

Table I shows that the apparent moment of diphenylmercury in benzene at 20° is lower than it appears to be in not-so-dilute carbon tetrachloride solution. Assuming that the behavior in the latter medium approaches that in the gas phase the solvent effect in benzene may be called negative. According to the opinions of several workers (5, p. 47), this effect is expected when the molecule contained in a cavity of polarizable solvent has its moment axis in the long dimension of the molecule. This description may apply to a bent molecule with mercury at one end of the dipole.

However, the situation at 20° is reversed at 40° where the moment in benzene is much higher than in carbon tetrachloride. In the absence of any prior opinions (5) about dependence of solvent effect on temperature we suggest that the change of molecular shape within the polarizable solvent cage may be due to C-Hg-C bond angle variation with respect to temperature. While this effect should not be profound, it must be remembered that throughout this argument we are considering moment variations which do not exceed 0.5 debye unit.

It would seem that dioxane is intermediate in behavior between the other two solvents. Indeed the concentration effect and the solvent polarizability effect may largely be compensated in dioxane. In this connection we point again to the intersections of Fig. 3. It is unfortunate that a vapor-phase moment value at this temperature (about 25°) is not available.



In any circumstance the data for diphenylmercury in the several solvents must be interpreted in terms of some type of induced polarization. This interpretation implies a definite dipole moment, even when it is very small (experimentally there are no negative moment values in very dilute carbon tetrachloride). The moments may be ascribed to C-Hg-C angularity and some of the differences may be due to variations in this angle. Evidence for differences in this angle will be presented in the remainder of this report.

Paradisubstituted Methylmercuribenzenes

If one assumes that benzene substituents are bonded coplanar with the ring then evidence of orientation polarization in a 1,4-dimercuribenzene ought to establish an angularity of bonding to mercury. To this end we have prepared 1,4-methylmercuri-*bis*-benzene (IIIa or b, R = H) by reaction of methyl chloride Grignard reagent with the 1,4-dibromomercuribenzene (II, R = H) derived from mercuric bromide and 1,4-bromo-magnesium-*bis*-benzene (I, R = H).

Although the product III has a tendency toward disproportionation to dimethylmercury and a polymer it is sufficiently stable for determination of its electrical polarization at 20° in carbon disulphide. This polarization should have no orientation component if the methylmercuri group were included in the plane of the ring or if the conformation were entirely IIIa (R = H). On the other hand the substance ought to show evidence of moment if the conformation IIIb were contributory. When the additive electronic polarization (used because III will decompose partially during the time required for determination of the dielectric constant of the solid) is subtracted from the total polarization, the difference may be calculated as a moment of 0.91 debye unit.*

A further test of non-linearity has been accomplished with 1,4-methylmercuridurene (IIIa or b, R = Me). This substance has been synthesized by mercuration of durene (IV, R = Me), and treatment of the product II (R = Me) with methyl chloride Grignard reagent. The product III, R = Me, is only a little less prone toward disproportionation than the simpler homologue. From the total polarization in carbon disulphide at 20° is subtracted the electronic polarization, again calculated additively. The remainder represents an electric moment of 1.38 debye unit.

In order to compare the moments of the two 1,4-disubstituted phenylene mercurials it is necessary to assign a group moment to methylmercuri. Although we realize the limitation of group moment evaluations, we have used 1-bromo-4-methylmercuribenzene (VIII, R = H, X = Br) obtained by treatment of 1-bromo-4-bromomercuribenzene (VII, R = H) with methyl chloride Grignard reagent. Actually VII is a by-product in the preparation of II as a consequence of the partial Grignardization (VI) of 1,4-dibromobenzene (V, R = H).

The moment of VIII, calculated from additive electronic polarization, in carbon disulphide at 20° is 1.94 debye unit. If a value (m_1) of 1.5 debye is assumed (excluding mesomeric effects) for the 4-bromophenyl group then an equation in two unknowns, the methylmercuri moment (m_2) and its angular deviation from linearity (α), may be formulated

$$(1.94)^2 = (1.5)^2 + (m_2)^2 - 2(1.5)(m_2) \cos \alpha.$$

*The disproportionation of the *bis*-mercurials described in this report is sufficiently slow that reliable polarization measurements can be made. This reliability has been demonstrated by recovery of the substance after the polarization measurement. However, the time required for analyses to be made elsewhere is detrimental. Additionally the high percentage of mercury in such compounds makes the results non-definitive. Consequently we have chosen to characterize the *bis*-mercurials analytically by quantitative conversion to the chloromercuri derivatives rather than by analysis of the elements.

If one now combines this equation algebraically with the equation which defines the moment of 1,4-methylmercuri-*bis*-benzene (III, R = H)

$$(0.91)^2 = \sqrt{2} \cdot m_2 \cdot \sin \alpha,$$

then assuming that the methylmercuri group moment and the moment angle α are the same in both compounds, two sets of values may be calculated. One value ($m_2 = 0.72$ debye unit; $\alpha = 62^\circ$) seems to be more probable than the other ($m_2 = 3.37$ debye unit, $\alpha = 10.9^\circ$) because the methylmercuri moment ought to be much lower than the group moment (3.5 debye unit) assigned previously to the chloromercuri group (6). Actually the more probable moment value is in approximate agreement with that expected in consideration of the polarizations of diphenylmercury and dimethylmercury. Likewise the C-Hg-C angle (180° minus 62°) is comparable with that estimated for the aliphatic *bis*-mercurials described below.

It is of interest to compare the moments of methylmercuri-*bis*-benzene and the homologous durene. If the C-Hg-C linkage were linear then the moments of both compounds (III, R = H or Me) ought to be identically zero. Actually the moment of the durene (1.38 D) is found to be $\sqrt{2}$ times that (0.91 D) of the benzene. If the substituents in 1,4-methylmercuri-*bis*-benzene are simple-harmonically rotating then this ratio specifies that the substituents in the homologous durene (III, R = Me) are hindered from free rotation. Moreover, the ratio indicates that the hindrance retains the methylmercuri group on one side of the ring (IIIb, R = Me), since any contribution from IIIa (R = Me) would decrease the ratio.

This "on-side" conformation is not unexpected in view of recent observations in respect of the moment of 1,4-dinitrobenzene (7). On the other hand it must be realized that quantitative estimations of this sort are unjustified, despite their common use, and the $\sqrt{2}$ relationship may be fortuitous. For example the group moment and moment angle may differ among the compounds, the bond angle may differ from the moment angle, and the assumption of planarity of the aromatic rings with coplanarity of the substituent methyl groups is nowadays equivocal. However, the quantitative estimation does accentuate the qualitative fact that the observed moments establish the non-linearity of the C-Hg-C linkage.

Aliphatic bis-Mercurials

The electrical polarization data for a series of aliphatic *bis*-mercurials is shown in Table II. It may be seen by reference to the three solid substances with which the combined electronic-plus-atomic polarizations can be determined that the additive values for electronic polarization are not greatly in error. In no instance can a zero moment be designated. Even the polarization of hexafluorodimethylmercury in carbon tetrachloride is appreciable (ca. 0.3 D), although the range of concentrations ($\omega = 0.0008$ to 0.0025) is comparable with that of diphenylmercury in carbon tetrachloride where no orientation polarization can be detected.

The trend in moment among the homologous series (methyl > ethyl > propyl) is not very informative except for the unexpectedly low moment of hexafluorodimethylmercury.* In view of the high polarity of the C-F linkage a much higher polarization than has been observed, irrespective of the polarity (necessarily low) of the mercury-carbon

*We are indebted for this compound to Mr. D. Fishel, Ohio State University, who prepared it from trifluoromethyl iodide and cadmium amalgam by the procedure of Emeleus and Haszeldine (8).

linkage, would have been expected. In the absence of this difference one may assume that the C-Hg-C angular relationship is variable in respect of the polarity of the substituent groups.

TABLE II
POLARIZATION DATA, ALIPHATIC *bis*-MERCURIALS, R_2Hg

| R_2Hg | Solvent | Temp., °C | P_{total} , cc | P_{e+at} , cc | P_e additive cc | μ , D |
|--------------------------------------|----------------------|--------------|---------------------|--------------------|----------------------|-----------|
| $(CH_3)_2Hg$ | Dioxane | 20 | 33.3 | — | 22.6† | 0.71 |
| | Benzene | 20 | 32.7 | — | 22.6 | 0.69 |
| | Benzene | 40 | 33.8 | — | 22.6 | 0.74 |
| $(CF_3)_2Hg$ | Benzene | 20 | 47.3 | 27.5* | 24.7 | 0.97 |
| | CCl_4 | 20 | 29.2 | 27.5 | 24.7 | 0.29 |
| $(C_2H_5)_2Hg$ | Benzene | 20 | 38.1 | — | 31.9 | 0.55 |
| $(n-C_3H_7)_2Hg$ | Benzene | 20 | 47.3 | — | 41.1 | 0.54 |
| 1,7-Dioxo-4,10-mercuro-cyclododecane | Benzene | 20 | 91.0 | 65.7‡ | 62.6 | 1.17 |
| Mercuracyclohexane | Benzene | 20 | 49.8 | — | 34.3 | 0.86 |
| Mercuracycloheptane | Carbon disulphide | 20 | 56.0 | — | 38.9 | 0.90 |

*Density at 22°, 4.693.

†Additive atomic constant for mercury, 11.2 cc, as determined by Wilde.

‡Density at 22°, 3.30.

The effect of temperature on the polarization of dimethylmercury in benzene has been examined briefly. The apparent augmentation of moment with increasing temperature is similar to that found for diphenylmercury in the same solvent, but is so slight (0.05 debye unit from 20 to 40°) that it might be ascribed to experimental error. However the difference is substantiated by comparison of the moment of diethylmercury (0.55 D at 20° in benzene) with that (0.39 D) reported in the same solvent at 14.5° (1).

In view of the evidence for a C-Hg-C angularity in these aliphatic *bis*-mercurials we have sought to examine analogues in which the angularity would be intrinsic in the structure. Of the last three items in Table II the first was once thought to be 1-oxa-4-mercuracyclohexane (9) but Grdenic proved by X-ray diffraction studies (10) that it is the dimer, 1,7-dioxo-4,10-mercuracyclododecane. Because of the flexibility of a 12-membered ring and also because of a possible tendency toward co-ordination of mercury with oxygen, the substance is not the ideal example we sought for examination of rigid angularity. Nevertheless a significant orientation polarization is observed which cannot be attributed alternatively to an abnormal atom polarization. At most the latter cannot exceed 3 cc, according to the value which we have obtained for the dielectric constant of the solid substance.

When 1,5-dichloromercuripentane is treated with sodium stannite the dimer of mercuracyclohexane is formed exclusively, and this dimer seems to be the stable form. However, by treatment of 1,5-dibromopentane with sodium amalgam in ethyl acetate (11) the monomer may be obtained in varying yield. Although this monomer, $C_5H_{10}Hg$, tends to transform easily to the dimer or polymer, it may be purified for immediate use by avoidance of elevated temperatures. The moment calculated from the electric polarization in benzene (0.86 D at 20°) is closely comparable with the moments of the non-cyclic *bis*-mercurials shown in Table II.

Application of Hilpert and Gruttner's method for the preparation of mercuracyclopentane (13, 12) yields only one product which seems to be the dimer, according to an isopiestic determination of molecular weight. Since the same product is obtained by

various reductions of 1,4-dichloromercuributane it would seem that monomeric mercuracyclopentane is too unstable for isolation in sufficient purity for electric polarization studies. The polarization of the dimer (probably 1,6-dimercuracyclodecane, since it can be reconverted to 1,4-dichloromercuributane by treatment with mercuric chloride) has not been measured.

The preparation of monomeric mercuracycloheptane has been more successful, and leads from either 1,6-dibromohexane or 1,6-dichloromercurihexane to a single product which is monomeric according to isopiestic molecular weight determinations (15, 14). The product can be reconverted to 1,6-dichloromercurihexane by means of mercuric chloride. Its moment is not strictly comparable with that of mercuracyclohexane because it has been necessary to use carbon disulphide as the solvent. However, the observed moment at 20° (0.9° D) is almost identical with that of mercuracyclohexane.

From these results it would seem that the C-Hg-C angle must be greater than 108–110°, but it may be as low as 120–130° in a stable configuration. Moreover, since the observed moments are less than twice as great as that of the comparable diethyl- and dipropyl-mercury the C-Hg-C angles in the latter substances need not exceed 150°.

But this estimate should not be construed to imply a fixed C-Hg-C angle for *bis*-mercurials. Indeed the apparent anomalies which have been observed by variation of temperature and solvent with diphenyl- and dimethyl-mercury, and also the lack of correlation of moment with polarity of substituents, is a strong indication that the C-Hg-C angle is widely variable. Perhaps this variability ought to be expected with a large atom-like mercury. Conversely one might say that mercurials are poor candidates for stereochemical studies. On the other hand the behavior of *bis*-mercurials may predict the day of better precision in measurement when no polyatomic substance is known that will not be oriented by an electrical field.

The authors are grateful for studentship aid and direct grants from the National Research Council of Canada which supported this research. They wish to thank Mrs. L. Westland and Mr. F. Lautenschlaeger for aid in the experimental work. Any experimental data not presented in the paper is available in the doctoral thesis of H. Sawatzky.

EXPERIMENTAL*

1,4-Chloromercuri-bis-durene

A mixture of 5.40 g (0.04 mole) of durene, 51.2 g (0.16 mole) of mercuric acetate, 40 ml of acetic acid, and 120 ml of methanol were refluxed for 4 days. The precipitated solid was removed by hot filtration and was washed with boiling ethanol, 11.7 g. This acetoxymercurial was then dissolved in 300 ml of hot acetic acid and the partially cooled system was treated with a solution of 10 g (0.17 mole) of sodium chloride in 50 ml of water. The solid product was filtered off and washed with boiling ethanol, 11.38 g (47%). It may be crystallized from pyridine but has no melting point. X-Ray diffraction pattern is [10] 7.59; [5] 4.45; [4] 3.97; [3] 2.85; [2] 3.52, 3.33, 2.96; [1] 4.63, 3.84, 3.21, 3.01, 2.63. Anal. Calc. for $C_{10}H_{12}Hg_2Cl_2$: C, 20.0; H, 2.01. Found: C, 20.3; H, 2.00.

1,4-Methylmercuri-bis-durene

Into 15 ml (0.0189 equiv.) of stirred methyl chloride or iodide Grignard reagent under nitrogen was added 2.00 g (0.0033 mole) of 1,4-chloromercuri-*bis*-durene. To the warm

*Melting points have been corrected against standards according to Can. J. Technol. **34**, 89 (1956). X-Ray diffraction is reported at relative intensities I/I_1 at d spacings in angstroms using $CuK\alpha$ (Ni filtered) radiation.

suspension was added 20 ml of dry diethyl ether. After 18 hours of stirring the system was poured on 50 g of crushed ice. Then 1% aqueous sulphuric acid was added until the system was slightly acidic. After evaporation of the ether the solid (1.47 g) was filtered off and almost dissolved in hot benzene. Evaporation of the filtered solution left 1.35 g (73%) of product which did not melt. Purification may be effected by crystallization from hot benzene (25 ml per g) but prolonged heating will cause disproportionation. X-Ray diffraction pattern is [10] 7.65; [9] 3.50; [6] 6.83; [5] 4.38; [4] 5.05; [3] 4.68, 4.03, 3.64, 2.26; [2] 2.92, 2.71; [1] 6.30, 3.35. In carbon disulphide α is 0.66 and β is 0.409, so P_{20} is 116.9 cc. With $R_D = 76.4$ cc, the moment is 1.38 D. Anal. Calc. for $C_{12}H_{13}Hg_2$: C, 25.6; H, 3.22. Found: C, 25.7; H, 3.25.

When a benzene solution of this material was treated with 2 mole equivalents of mercuric chloride in ether a white precipitate could be filtered off after 20 minutes. When this precipitate (88.7% after ether washing) was treated with bromine in aqueous potassium bromide it was converted to 1,4-dibromodurene, m.p. 200–203°. The benzene filtrate left methylmercuric chloride (83%, m.p. 164–168°) when it was evaporated.

1,4-Methylmercuri-bis-benzene

To a stirred suspension of 2.40 g (0.1 atom) of magnesium in 50 ml of dry ether was added 2 ml of ethyl bromide in 50 ml of ether during 30 minutes. Then a solution of 4.72 g (0.02 mole) of *p*-dibromobenzene and 3.85 ml (total 0.06 mole) of ethyl bromide in 100 ml of ether was added during 75 minutes. Strong reflux was maintained and continued during 12 hours, then 1.2 ml more of ethyl bromide was added. After 1 hour all the magnesium was consumed, so 27.2 g (0.1 mole) of mercuric chloride was introduced during 24 hours from a soxhlet extractor.

The solid product was filtered off and washed thoroughly with water, boiling ethanol, and boiling benzene. There remained 4.88 g (38%) of 1,4-bromomercuribenzene, identified by conversion in 93% yield to 1,4-diiodobenzene, m.p. 127–129°, by means of iodine in an alcoholic suspension of the mercurial.

The filtrate from which this product was obtained was evaporated and then steam-distilled to remove 11.9 g of ethylmercuric bromide. The residue yielded 1.96 g (23% as *p*-bromophenylmercuric bromide) which may be crystallized from benzene, m.p. 234–236°. It has been converted to *p*-bromophenylmercuric acetate, m.p. 198–201°, by means of silver acetate, and subsequently to *p*-bromophenylmercuric chloride, m.p. 251–253°, by means of sodium chloride (16). Also it was converted quantitatively to *p*-dibromobenzene by treatment with bromine in aqueous potassium bromide.

To a stirred suspension of 1,4-bromomercuri-bis-benzene (4.30 g, 0.0074 mole) in 25 ml of dry ethyl ether at 0° under nitrogen was gradually added 20 ml (0.02 equiv.) of Grignard reagent from methyl chloride or iodide. After subsequent stirring for 90 minutes the system was poured onto 200 g of crushed ice. The ether was evaporated and the remainder was extracted by 100 ml of pure carbon disulphide. Evaporation of the extract left 2.26 g (61% of the bromomercuri-bis-benzene) which was crystallized from 50 ml of 1:1 benzene – diethyl ether. The melting point of this methylmercuri-bis-benzene is 190–193° with decomposition at 185° indicating disproportionation. It does not contain halogen; X-ray diffraction pattern is [10] 4.56; [3] 3.75, 3.63, 3.34, 3.21; [2] 5.92, 5.23; [1] 5.62. In carbon disulphide α is 0.29 and β is 0.460 so P_{20} is 75.7 cc. If R_D is 57.9 cc the moment is 0.91 D.

Although a satisfactory elemental analysis was not obtained the methylmercuri-bis-benzene was analytically characterized when a suspension of 0.044 g (0.00087 mole) in

1 ml of ethyl ether was shaken for 3 hours with a solution of 0.047 g (0.018 mole) of mercuric chloride in 5 ml of ether. The solid was filtered off and ether-washed, 0.047 g (98%) of 1,4-chloromercuri-*bis*-benzene which was converted quantitatively to 1,4-dibromobenzene. Anal. Calc. for $C_6H_4Hg_2Cl_2$: Cl, 12.93. Found: Cl, 12.97. The ether filtrate was evaporated to yield 0.0441 g (100%) of methylmercuric chloride, m.p. 168–170°, after crystallization from ethanol.

1-Bromo-4-methylmercuribenzene

A suspension of 0.87 g of *p*-bromophenylmercuric bromide (0.002 mole, obtained from the experiment reported above) in 25 ml of diethyl ether was stirred and ice-cooled under nitrogen, while 3.50 ml (0.0033 equiv.) of Grignard reagent from methyl chloride was added during 5 minutes. After 3 hours of subsequent stirring at ice-bath temperature the system was poured onto 75 g of crushed ice. The non-aqueous phase, dried by magnesium sulphate, was evaporated to leave an oil (0.63 g, 82%) which solidified when chilled to 4°. It was twice crystallized by solution (at 25°) in 1:1 ethanol-chloroform (32 ml per g) and subsequent chilling to –78°. The purified product, m.p. 52.1–52.7°, was characterized by cleavage with mercuric chloride, yielding methylmercuric chloride and *p*-bromophenylmercuric chloride, each in 100% yield. The Grignard reagent from methyl iodide cannot be used in this preparation because disproportionation occurs. In carbon disulphide this mercurial has $\alpha = 2.01$ and $\beta = 0.436$ so $P_{200} = 122.9$ cc, and $\mu = 1.94$ D if $R_D = 49.9$ cc.

Mercuracycloheptane

A mixture of 450 g (0.195 atom Na) of 1% sodium amalgam, 16.5 g (0.07 mole) of 1,6-dibromohexane, 3 ml of ethyl acetate, and 25 ml of benzene was shaken at 70° (infrared lamp) for 1 day, after which time 25 ml each of benzene and water was added with agitation. After separation of the non-aqueous phase a subsequent extraction with 25 ml of benzene was accomplished. Evaporation of the benzene left 7.6 g of oily solid which was purified first by three crystallizations from chloroform (3 ml per g) from 25° to –78° and then by repeated crystallization from 4:1 ether-benzene and from 1:5 ethanol-benzene (3 ml per g) to melt at 58.5–60.2°. Anal. Calc. for $C_6H_{12}Hg$: Mol. wt., 285. Found (Willard and Blank (15)): Mol. wt., 273. Found (Barger-Rast (14)): Mol. wt., 286.

1,6-Dichloromercurihexane

A solution of 2.84 g (0.01 mole) of mercuracycloheptane in a minimum of benzene was treated with 2.72 g (0.01 mole) of mercuric chloride and then 10 ml of ethyl ether was added. The white suspension formed by stirring was filtered off and washed thoroughly with ether, 5.60 g (100%) of 1,6-dichloromercurihexane. Anal. Calc. for $C_6H_{12}Hg_2Cl_2$: Cl, 12.75. Found: Cl, 12.69. After crystallization from hot dimethylsulphoxide (15 ml per g) it melts questionably at 290° with decomposition. The X-ray powder diagram is [10] 11.72; [9] 3.31; [7] 2.65; [5] 2.38; [2] 2.99; [1] 2.25, 3.99, 4.44. Reduction of this high-melting mercurial by alkaline sodium stannite forms mercuracycloheptane, m.p. 58–60°, in 90% yield. Identity was established by mixture melting point.

Mercuracyclohexane

A mixture of 15 g (0.065 mole) of dibromopentane, 450 g (0.2 atom) of 1% sodium amalgam, 3 ml of ethyl acetate, and 50 ml of dry benzene was shaken in a stout sealed bottle at 75° for 24 hours. After treatment with 100 ml of cold water the spent amalgam

was separated and washed with 50 ml each of water and benzene. The benzene solutions, adequately dried, were vacuum evaporated leaving 8.20 g of oil. This oil was twice extracted by 5-minute reflux with 25 ml of absolute ethanol. The quickly cooled extract was filtered and further chilled to 40°. Slowly there appeared 0.53 g of crystals. Contrary to Hilpert and Gruttner the substance was found only in the extract. Three rapid crystallizations from a benzene-hexane mixture gave a product, m.p. 122.4–122.8°. The monomer seems to be very unstable thermally, and sometimes is not obtainable.

When this product was treated with mercuric chloride, a quantitative yield of 1,5-dichloromercuripentane was obtained. The X-ray diffraction pattern of this *bis*-chloromercurial is: [10] 4.33; [9] 3.34; [8] 3.18; [7] 3.56; [6] 1.97; [5] 2.71; [3] 2.11; [2] 2.45, 2.35, 2.30, 2.07; [1] 2.86, 2.17, 1.82, 1.78. Regeneration of the *bis*-mercurial by treatment with sodium stannite yielded only the dimer described by Hilpert and Gruttner (11). The monomeric *bis*-mercurial decomposed in boiling ethanol to yield an oil which seems to contain the dimer.

1,6-Dimercuracyclodecane

(a) *From dibromobutane*.—A mixture of 450 g (0.2 mole) of 1% sodium amalgam, 15.3 g (0.07 mole) of 1,4-dibromobutane, 3 ml of ethyl acetate, and 25 ml of benzene was shaken for 36 hours at 70°. The cooled system was then shaken with 25 ml of water and the benzene layer was separated and combined with a subsequent 25 ml benzene washing. Evaporation left an oil, 10.79 g, which was washed with cold ether leaving 3.79 g of sticky solid. Crystallization from an ether-benzene mixture gave a product, m.p. 44–45.2°.

(b) *From 1,4-dichloromercuributane*.—A sample of 0.50 g (10^{-4} mole) of 1,4-dichloromercuributane was treated with 40 ml of 10% aqueous sodium hydroxide and then with a solution of 1 g of stannous chloride dihydrate in 20 ml of 20% aqueous sodium hydroxide. The black suspension was filtered off when no more color change occurred. The black product was extracted with boiling xylene which was evaporated at low temperature leaving 0.17 g (66%) m.p. 37–40°. Crystallization from ether-benzene raised this melting point to 43–45°. Molecular weight determinations by the isopiestic method of Willard and Blank gave an average value of 499, while a freezing-point depression in diphenylmercury gave a value of 517. The calculated molecular weight is 513.

1,4-Dichloromercuributane

When 0.1294 g (253×10^{-6} mole) of dimercuracyclodecane in benzene is treated with 0.1390 g of mercuric chloride dissolved in a minimum of ethyl ether the resulting precipitate, washed with benzene and ether, weighs 0.253 g (93%). Its X-ray diffraction pattern is [10] 3.18; [9] 4.61; [7] 2.09; [5] 2.62; [4] 2.41; [3] 3.55, 1.78; [2] 2.53; [1] 4.00, 3.47, 2.49, 2.03 after crystallization from hot dimethylsulphoxide; m.p. 292–293° (with decomposition). Anal. Calc. for $C_4H_{10}Hg_2Cl_2$: Cl, 13.5. Found: Cl, 13.3.

Dialkylmercury Homologues

These mercurials were prepared from alkylmercuric halides according to the following general procedure. The alkylmercuric halide (0.026 mole) was dissolved and suspended in 150 ml of 10% aqueous sodium hydroxide. A solution of 8.33 g (0.035 mole) of stannous chloride dihydrate in 100 ml of aqueous sodium hydroxide was added. After 3 hours of agitation the system was steam-distilled (methyl and ethyl) or ether-extracted (propyl and butyl). All were dried with magnesium sulphate over an ether solution or (methyl)

directly by potassium hydroxide pellets and then distilled. All except dimethylmercury (m.p. -42.8 to -41.9°) are unstable in light and dibutylmercury is unstable to heat.

PHYSICAL PROPERTIES OF DIALKYL MERCURY HOMOLOGUES

| Alkyl | Boiling point, $^\circ\text{C}$ | mm | n_D^{20} |
|------------------|------------------------------------|------|------------|
| Methyl | 90.7-91.1 | 755 | 1.54512 |
| Ethyl | 50-51 | 16 | 1.54541 |
| <i>n</i> -Propyl | 80.0-80.6 | 16.5 | 1.51755 |
| <i>n</i> -Butyl | 67 | 0.55 | 1.50812 |
| | 48 | 0.35 | |

Other bis-Mercurials

Diphenylmercury was dissolved in hot 93% ethanol (40 ml per g) and allowed to cool very slowly with stirring, m.p. 125 – 126° . The purification of 1,7-dimercura-4,10-dioxacyclododecane (10) was effected by crystallization from chloroform, m.p. 145 – 146° , and its dielectric constant at 22° was found to be 2.975. Hexafluorodimethylmercury as received from Mr. Fishel was sublimed at 85 – 95° and 750 mm until the melting point was constant at 166 – 166.5° .

Purification of Solvents

Benzene was purified according to a previous description (17) and was stored over sodium under nitrogen, $\epsilon = 2.284$ and $d = 0.8788$ at 20° . Dioxane, prepared as was described previously (17), was stored under nitrogen without sodium, $\epsilon = 2.224$ and $d = 1.0336$ at 20° . Carbon disulphide was thrice-stirred during 2 hours with 100 ml of 2.5% aqueous potassium permanganate per liter, then for 5 hours with metallic mercury (250 g per liter), and finally with 2.5% aqueous mercuric chloride (100 ml per liter). After drying with phosphorus pentoxide the solvent was distilled and stored under nitrogen in the dark, $\epsilon = 2.646$ and specific volume = 0.79135. Like dioxane it is unstable. The purification of 11 liters of carbon tetrachloride was accomplished by the method of Ingold and Powell (18) by digestion at 50 – 60° for 3 hours with 750 ml of Fehling's solution. The non-aqueous layer was then refluxed with 5% aqueous sodium hydroxide for 3 hours, then washed with water and stirred about 15 times with 100-ml lots of concentrated sulphuric acid until coloration ceased. After being washed with aqueous sodium carbonate the carbon tetrachloride was azeotropically distilled to remove most of the water. Then it was dried with phosphorus pentoxide, distilled, and stored under nitrogen in dark bottles, $\epsilon = 2.2415$ and $V = 0.62730$ at 20° .

Dielectric Constants of Solutions

All determinations were made at 500 kc in the apparatus described previously (19). Except for the studies with diphenylmercury in carbon tetrachloride no experiment was accepted if the individual determinations did not permit linear plots of $d\epsilon/d\omega$ (α) and $dV/d\omega$ (β). Moreover, no experiment was accepted in which the extrapolations of α and β to zero concentration differed more than ± 0.0002 in specific volume and ± 0.002 in dielectric constant from the values tabulated as follows.

Dielectric Constants of Solids

The method described previously (17, 20) has been followed. The pellet thickness was measured after the determination at 5 Mc by averaging the gauged value at 4

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF PURE SOLVENTS

| Solvent | 20° | | 25° | | 30° | | 40° | |
|----------------------|------------|--------|------------|---------|------------|--------|------------|--------|
| | ϵ | V | ϵ | V | ϵ | V | ϵ | V |
| Benzene | 2.2849 | 1.1381 | — | — | 2.2612 | 1.1524 | 2.2395 | 1.1670 |
| Dioxane | 2.2206 | 0.9675 | — | — | — | — | 2.1851 | 0.9900 |
| Carbon disulphide | 2.6470 | 0.7911 | — | — | — | — | — | — |
| Carbon tetrachloride | 2.2426 | 0.6273 | 2.2306 | 0.6313 | — | — | 2.1986 | 0.6436 |
| | 2.2380 | 0.6270 | 2.2272 | 0.6310* | — | — | 2.1962 | 0.6435 |

*The final six values are the best obtained for CCl_4 to date.

quadrants of the cylinder; also oftentimes the pellet was broken into halves and the center measured as well. A redetermination of the dielectric constant of diphenylmercury pellets gave a value of 57.1 cc, thus confirming the previously reported value (19).

Infrared Spectrum of Diphenylmercury

Only three absorption bands were found in the 900–300 cm^{-1} spectral region for a 10% solution of diphenylmercury in benzene, although the strong absorption of the solvent at 680 cm^{-1} may have obscured the behavior of diphenylmercury in this frequency range. The bands at 732 cm^{-1} (80% absorption) and 706 cm^{-1} (40% absorption) were symmetrical and well resolved, but the band at 463 cm^{-1} (30% absorption) was unsymmetrical, showing evidence of perturbations on the low frequency side. This band also is of interest because of its possible relationship to the angle of swing postulated by deLazlo (21) for *bis*-bromophenylmercury.

Organomercuric Halides

With the exception of the first and fourth items of Table III these substances were prepared by cleavage of *bis*-mercurials by means of mercuric chloride in ether solution. The methylmercuric chloride was crystallized (13 ml per g) from 95% ethanol, m.p. 168.7–169.6°. The ethyl analogue from 1:1 benzene–carbon tetrachloride melted at 191.8–192.9°. The propyl homologue from 95% ethanol (15 ml per g) melted at 141–143° but after sublimation melted at 142.1° to 142.7°. The butyl homologue crystallized from benzene (5 ml per g) to melt at 125.5–126.2° and then from 95% ethanol (15 ml per g) to melt at 126.9–127.2°.

The preparation of chlormethylmercuric chloride was carried out according to Hellerman and Newman (22). The 97.5% yield was crystallized from ethanol, m.p. 128.5–130°. The X-ray diffraction is [10] 10.59, 3.22; [8] 4.05, 3.26; [6] 2.65, 2.62; [4] 1.90; [2] 2.35, 3.52; [1] 4.87, 2.93, 2.43, 2.00. It is of interest that the compound also may be obtained by the action of diazomethane on 2-hydroxyorganomercuric halides.

These chloromercurials were prepared to demonstrate that the R–Hg group becomes more electropositive with increasing size in the normal homologous series. This behavior is shown in Table III.

TABLE III
POLARIZATION DATA, ORGANOMERCURIC HALIDES, R_2HgCl

| R | Solvent | α | β | P_{20}, cc | R_D, cc | μ, D |
|-----------------------|---------|----------|---------|---------------------|------------------|-----------------|
| <i>p</i> -Bromophenyl | Dioxane | 1.32 | 0.690 | 114.8 | 50.1 | 1.75 |
| Methyl | Dioxane | 6.02 | 0.740 | 261.3 | 22.9 | 3.36 |
| Ethyl | Dioxane | 6.80 | 0.778 | 306.9 | 27.5 | 3.64 |
| Chloromethyl | Dioxane | 3.80 | 0.723 | 197.9 | 27.8 | 2.84 |
| <i>n</i> -Propyl | Benzene | 5.60 | 0.822 | 315.9 | 32.1 | 3.67 |
| <i>n</i> -Butyl | Benzene | 5.94 | 0.750 | 357.7 | 36.8 | 3.90 |

A study of the dielectric constants of these solid organomercurials is in progress with a view to clarify the discrepancy between the $P_{\epsilon+g}$ values which we have measured versus the calculated values which appear in the literature (23).

REFERENCES

1. BERGMANN, E. and SCHÜTZ, W. *Z. physik. Chem. B*, **19**, 401 (1932).
2. HAMPSON, G. C. *Trans. Faraday Soc.* **30**, 877 (1934).
3. ARMSTRONG, R. S., LEFEVRE, C. G., and LEFEVRE, R. J. W. *J. Chem. Soc.* 371 (1957).
4. SIPOS, J., SAWATZKY, H., and WRIGHT, G. F. *J. Am. Chem. Soc.* **77**, 2759 (1955).
5. SMYTH, C. P. *Dielectric behavior and structure*. McGraw-Hill Book Co., Inc., New York, 1955. p. 39.
6. CURRAN, B. C. *J. Am. Chem. Soc.* **64**, 830 (1942).
7. PODLESCHKA, P., WESTLAND, L., and WRIGHT, G. F. *Can. J. Chem.* **36**, 574 (1958).
8. EMELEUS, H. J. and HASZELDINE, R. N. *J. Chem. Soc.* 2953 (1949).
9. SAND, J. *Ber.* **34**, 2913 (1901).
10. GRDENIC, D. *Acta Cryst.* **5**, 367 (1952).
11. HILPERT, S. and GRUTTNER, G. *Ber.* **47**, 177, 186 (1914).
12. VON BRAUN, J. *Ber.* **46**, 1792 (1913).
13. VON BRAUN, J. *Ber.* **47**, 491 (1914).
14. FRIEDRICH, A. *Die Praxis der quantitativen organischen Mikroanalyse*. F. Deiticke Co., Leipzig, 1933. p. 191.
15. SCHNEIDER, F. *Organic qualitative microanalysis*. John Wiley & Sons, Inc., New York, 1946. p. 118.
16. HANKE, M. E. *J. Am. Chem. Soc.* **45**, 1321 (1923).
17. MEREDITH, C. C., WESTLAND, L., and WRIGHT, G. F. *J. Am. Chem. Soc.* **79**, 2385 (1957).
18. INGOLD, C. K. and POWELL, W. J. *J. Chem. Soc.* 1222 (1921).
19. MEREDITH, C. C. and WRIGHT, G. F. *Can. J. Technol.* **33**, 182 (1955).
20. GEORGE, M. V. and WRIGHT, G. F. *Can. J. Chem.* **36**, 189 (1958).
21. DE LAZLO, H. *Trans. Faraday Soc.* **30**, 884 (1934).
22. HELLERMAN, L. and NEWMAN, M. D. *J. Am. Chem. Soc.* **54**, 2859 (1932).
23. STROHMER, W. *Z. Elektrochem.* **60**, 58 (1956).

THEORETICAL ASPECTS OF THE UNIMOLECULAR DECOMPOSITION OF NITROUS OXIDE¹

E. KERRY GILL AND KEITH J. LAIDLER

ABSTRACT

The kinetic data for the unimolecular decomposition of nitrous oxide, recently analyzed by Johnston, have been considered from the standpoint of the theories of unimolecular decompositions. Particular attention is paid to the high-pressure first-order rates, the low-pressure second-order rates, and the pressure range over which the rates fall off. A normal-mode analysis is made for the molecular vibrations, and calculations are made on the basis of N. B. Slater's theory. It is found that when the change of multiplicity is taken into account the Slater theory gives a satisfactory interpretation of the high-pressure behavior, but gives rates that are much too small in the low-pressure region. The theories of Hinshelwood, Kassel, and Rice and Ramsperger account more satisfactorily for the rate of activation, and Kassel's theory accounts for the pressure fall-off. A modified theory of unimolecular reactions is proposed to explain the observed results.

INTRODUCTION

The thermal decomposition of nitrous oxide is of very special interest, since the molecule is one of the simplest capable of undergoing unimolecular breakdown. The reaction is therefore particularly suitable for testing the various theories of unimolecular reactions that have been proposed. Until recently the experimental results for the reaction have been somewhat confusing, owing to various complications such as the existence of surface effects. However Johnston (1) has recently carried out a detailed critical analysis of the various results and has shown that when the complications are eliminated the reaction represents an excellent example of a straightforward unimolecular decomposition. It is possible that Johnston slightly oversimplifies the situation (2), but it seems likely that the rate constants he deduces for the high- and low-pressure reaction are close to the true ones. They should certainly be sufficiently reliable to permit a careful test of the theories, and this is what has been done in the present paper. A similar analysis of the hydrogen peroxide decomposition has also been carried out and will be published elsewhere (3) together with a more detailed treatment of mechanisms (4).

As far as the high-pressure behavior is concerned, all modern theories of unimolecular reactions lead to approximately the same conclusions. Hinshelwood's expression (eq. [4] below) for the rate of energization together with Kassel's equation for the rate of breakdown of a critically energized molecule leads to the result that the high-pressure first-order rate constant is

$$[1] \quad k_{\infty} = k^{\ddagger} e^{-\epsilon^*/kT},$$

where k^{\ddagger} is of the order of magnitude of a vibrational frequency in the molecule ($\sim 10^{13}$ sec⁻¹) and ϵ^* is the energy of activation per molecule. Slater's theory (5, 6, 7, 8, 9, 10, 11) leads to the similar result that

$$[2] \quad k_{\infty} = \bar{\nu} e^{-\epsilon^*/kT},$$

where $\bar{\nu}$ is a specially weighted average of the vibrational frequencies in the molecule. Eyring's absolute rate theory (12, 13) gives the relationship

$$[3] \quad k = \frac{kT}{h} \frac{f^{\ddagger}}{f} e^{-\epsilon^*/kT},$$

¹Manuscript received June 30, 1958.

Contribution from the Department of Chemistry, the University of Ottawa, Ottawa 2, Canada.

where kT/h is close to a vibration frequency and the ratio of partition functions f^\ddagger/f is usually close to unity. Frequency factors of 10^{13} sec^{-1} are therefore satisfactorily explained by all theories. Values significantly greater than this, of which there are a number of examples, are explained on the basis of eq. [3] in terms of a high value of f^\ddagger/f , which corresponds to a large positive entropy of activation. Modifications to equations [1], [2], and [3] are necessary when, as with nitrous oxide, the equation involves a change in multiplicity and therefore a small transmission coefficient.

As far as the low-pressure second-order behavior is concerned there are much wider divergences between the different theories of unimolecular reactions. This low-pressure rate is actually the rate of energization of the molecules, and there are two main expressions for this rate, corresponding to two fundamentally different definitions of energization. One of these expressions was first proposed by Hinshelwood (14) and has been employed in the subsequent theories of Kassel (15, 16) and of Rice and Ramsperger (17, 18). The definition of energization to which this expression applies is that the molecule contains, distributed amongst its s normal modes of vibration, at least the energy ϵ^* required for the reaction to occur. The rate of energization to this energy state is, to a good approximation,

$$[4] \quad k_1 = Z \frac{1}{(s-1)!} \left(\frac{\epsilon^*}{kT} \right)^{s-1} e^{-\epsilon^*/kT},$$

where Z is the collision number. Inherent in this treatment is the assumption that the energy can flow freely between the various modes so that provided the energy ϵ^* is in the molecule it may, after a sufficient number of vibrations, pass into one particular normal mode which is involved in the breakdown of the molecule.

In Slater's theory the contrary assumption is made that there can be no flow between the normal modes. Reaction occurs not when the energy gets into a particular mode but when the vibrations come suitably into phase, so that a critical co-ordinate becomes sufficiently extended. Not all molecules which are energized in the HKRR* sense are capable of undergoing reaction; only those which initially have the energy distributed in a particular way among the normal modes are capable of doing so. Slater's definition of energization is therefore a more stringent one than is HKRR's, and his expression for the rate of energization gives rise to much lower values. The expression is approximately

$$[5] \quad k_1 = Z (\epsilon^*/kT)^{\frac{1}{2}(n-1)} (4\pi)^{\frac{1}{2}(n-1)} \prod \mu_s e^{-\epsilon^*/kT},$$

where n is the number of normal modes concerned in the reaction and the μ 's are quantities that are related to the "amplitude factors" for the various normal modes. A rigorous test of Slater's theory can only be made by carrying out a detailed vibrational analysis, a matter of considerable difficulty for all except very simple molecules. Slater's theory has been applied quantitatively to cyclopropane, which isomerizes thermally into propylene, and the results were very satisfactory (8). With hydrogen peroxide, on the other hand, the calculated low-pressure rates were much smaller than the experimental ones (3).

In the present paper both the HKRR and Slater theories are applied quantitatively to the nitrous oxide decomposition. It will be seen that Slater's expression gives much too low a rate of energization, but that the theory provides a satisfactory formulation

*This abbreviation will be used to denote the point of view taken in the theories of Hinshelwood, Kassel, and Rice and Ramsperger.

for the first-order behavior. A more general treatment of unimolecular processes is outlined at the end of this paper.

THE EXPERIMENTAL DATA

Only the bare results will be stated here; for a more detailed discussion of the experimental work reference should be made to Johnston's paper (1). The rate-controlling step is believed to be



a reaction that is endothermic by 39.5 kcal. The high-pressure activation energy of the reaction is close to 60.0 kcal. At 888° K the high-pressure first-order rate constant is

$$k_{\infty} = 7.47 \times 10^{-4} \text{ sec}^{-1},$$

and this corresponds to a frequency factor of

$$8.134 \times 10^{11} \text{ sec}^{-1}.$$

By extrapolation of Johnston's second-order rate coefficients to zero pressure we estimate the rate of energization to be

$$k_1 = 14.0 \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

The pressure at which the first-order rate coefficient falls to one-half of its limiting value is approximately

$$p_{\frac{1}{2}} = 1.3 \times 10^4 \text{ mm.}$$

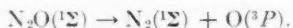
THEORY OF THE HIGH-PRESSURE RATES

The experimental frequency factor at high pressures, $8.134 \times 10^{11} \text{ sec}^{-1}$, is significantly below what would be expected on the basis of equations [1], [2], and [3] above. The frequencies of vibration of the molecule are of the order of 10^{13} sec^{-1} , so that k^{\ddagger} in Kassel's theory is of this magnitude. Slater's average vibrational frequency, weighted using the μ values derived below, is

$$\bar{\nu} = 4.50 \times 10^{13} \text{ sec}^{-1}.$$

The value of kT/h at 888° K is equal to $1.85 \times 10^{13} \text{ sec}^{-1}$. It is therefore seen that the experimental value is too low by between one and two powers of 10.

The reason for this lies in the fact that the rate-controlling step involves a change of multiplicity:



Since a triplet and a singlet can only give a triplet it follows that the reaction must involve a transition from one potential-energy curve to another, as represented schematically in Fig. 1. The ground state of N_2O correlates with $\text{N}_2({}^1\Sigma)$ and $\text{O}({}^1D)$, and the curve for this crosses the repulsive curve for $\text{N}_2({}^1\Sigma) + \text{O}({}^3P)$. The forms of these curves have been discussed by Stearn and Eyring (19). At the time their paper was published, however, the experimental evidence pointed to an activation energy as low as 52 kcal and a transmission coefficient of about 10^{-4} . This suggested a resonance splitting of as little as 5 cal per mole, and difficulty was experienced in explaining such a small value. The value of 10^{-1} to 10^{-2} obtained above leads to a resonance separation of the order of 500 cal per mole and this is what might reasonably be expected on the basis of spin-orbit interactions (19).

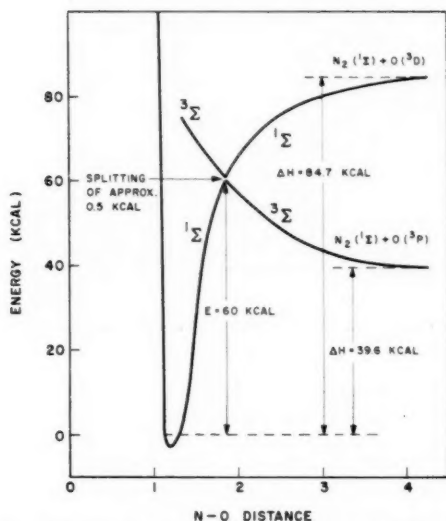


FIG. 1. Schematic potential-energy curves for the decomposition of nitrous oxide. The curves are based on those calculated by Stearn and Eyring, but are modified slightly to accommodate the latest thermochemical and kinetic values.

THEORY OF THE LOW-PRESSURE RATE

The low-pressure second-order rate constant, found experimentally to be about $14.0 \text{ cc mole}^{-1} \text{ sec}^{-1}$, is, according to all theories, the rate of energization of the molecule. This value must be explained in terms of the distribution of the energy of activation amongst the four normal modes of vibration, with or without flow of energy between the normal modes. In the calculations the collision diameter will be taken as $3.31 \times 10^{-8} \text{ cm}$, as employed by Johnston (1). At 888° K this corresponds to a collision number Z of

$$3.182 \times 10^{-10} \text{ cc molecule}^{-1} \text{ sec}^{-1} = 1.916 \times 10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

The HKRR Theory

With s equal to 2 and ϵ^* equal to $60.0 \text{ kcal per mole}$ the value of k_1 calculated using eq. [4] is $6.09 \text{ cc mole}^{-1} \text{ sec}^{-1}$, which is reasonably close to the experimental value of $14.0 \text{ cc mole}^{-1} \text{ sec}^{-1}$. This choice of s gives the best agreement; $s = 4$, for example, leads to $1.22 \times 10^3 \text{ cc mole}^{-1} \text{ sec}^{-1}$. The reason that $s = 3$ and $s = 4$ leads to rates that are too high is presumably that there is little flow of energy between the two axial and the two bending modes (see below).

Slater's Theory

A vibrational analysis for the N_2O molecule has been carried out, and the details are given in the Appendix. The molecule is linear and the normal modes of vibration are shown in Fig. 2. Two of the frequencies, ν_1 and ν_3 in the conventional notation, correspond to axial vibrations, and one frequency, ν_2 , corresponds to the doubly degenerate vibrations perpendicular to the axis. The motion of the molecule may be described in terms of three co-ordinates w , x , and y , of which w denotes the mutual displacement of the nitrogen atoms and x and y the components of the displacement of the oxygen atom relative to the center of the N-N distance; x is along the axis of the molecule and

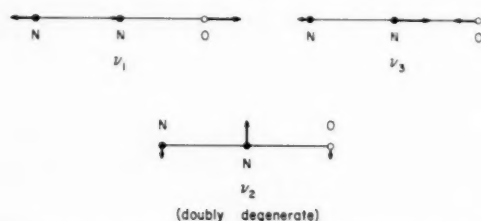


FIG. 2. The normal vibrations of nitrous oxide. The molecule is drawn to scale (equal N-N and N-O distances) and the vector lengths approximately represent the relative displacements.

y perpendicular to it. The analysis (cf. Appendix) leads to the result that the ratios of the displacements are:

$$\begin{aligned} \text{for } \nu_1 \quad x:w:y &= 1.00:0.429:0, \\ \text{for } \nu_2 \quad x:w:y &= 0:0:\text{constant}, \\ \text{for } \nu_3 \quad x:w:y &= -0.857:1.00:0. \end{aligned}$$

In applying Slater's theory we shall take as the critical co-ordinate for the dissociation into $N_2 + O$ the distance from the O to the center of mass of N-N. The variation in this co-ordinate, p , is equal simply to x ; it does not involve w and y . Since the bending vibrations involve only y it follows that they do not contribute to the decomposition, so that we must take n equal to 2.* The amplitude factors, α , and the corresponding μ 's, corresponding to the two axial vibrations are shown in Table I. The product of the μ 's is given by

$$[6] \quad \prod_k \mu_k = \mu_1 \mu_3 = 0.3824.$$

Using eq. [5] the value of k_1 is then found to be, with $n = 2$,

$$k_1 = 1.40 \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

This is below the experimental value by a factor of 10.

TABLE I
FREQUENCIES AND AMPLITUDE FACTORS (α AND μ) FOR THE TWO AXIAL MODES

| i | ν_i/sec^{-1} | α_i | μ_i |
|-----|-------------------------|--------------------------|---------|
| 1 | 3.864×10^{13} | 1.300×10^{-3} | 0.9066 |
| 3 | 6.709×10^{13} | -0.6048×10^{-3} | 0.4218 |

THE FALLING-OFF OF THE HIGH-PRESSURE RATE COEFFICIENT

Figure 3 shows the experimental first-order rate coefficients as a function of pressure. The two lines to the left show the theoretical behavior based on Kassel's theory (15, 16), with s equal to 2 and to 4. These curves were constructed by numerical integration of Kassel's general rate equation

*It is readily shown using Slater's procedures that the bending vibrations do not make a contribution for any choice of axial co-ordinate.

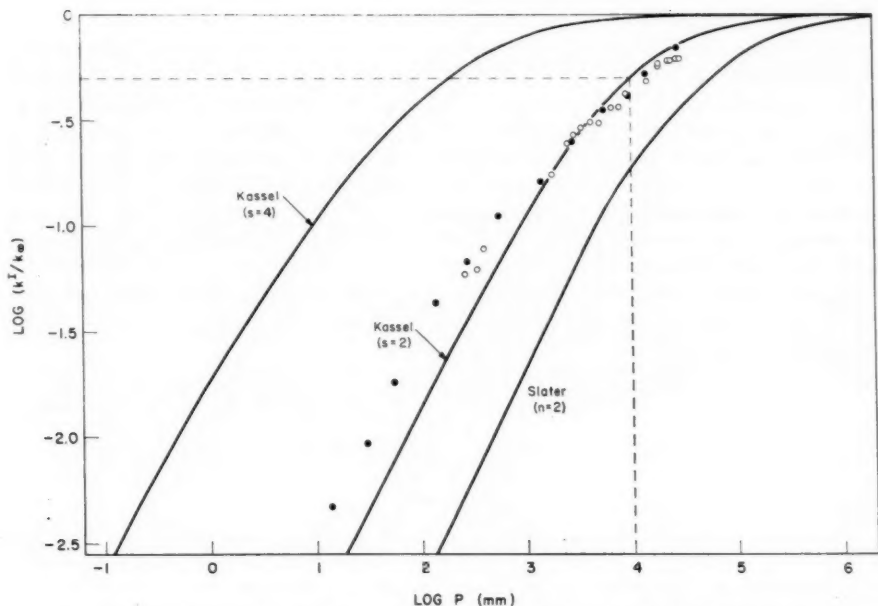


FIG. 3. Plot of the logarithm of the first-order rate coefficient against the logarithm of the pressure. The open circles represent the values given by Johnston (1), the closed circles values obtained by extrapolation. The calculated Kassel curve with $s = 2$ is seen to lie close to the experimental points, whereas Slater's curve gives rates that are too low except in the high-pressure region.

$$[7] \quad \frac{k^I}{k_\infty} = \frac{1}{(s-1)!} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + \frac{k^\ddagger}{k_{-1}[A]} \left(\frac{x}{b+x} \right)^{s-1}}$$

using the values

$$\begin{aligned} b &= 34.63, \\ k^\ddagger &= 7.47 \times 10^{-4} \text{ sec}^{-1} \text{ (experimental),} \\ k_{-1} &= 3.182 \times 10^{10} \text{ cc. molecule}^{-1} \text{ sec}^{-1}. \end{aligned}$$

The curve for $s = 4$ is shown to lead to rates that are much higher than the experimental ones, but that for $s = 2$ falls very close to the experimental values. The pressure for $s = 2$ at which k^I reaches one-half the limiting rate is 1.3×10^4 mm, and this is essentially the same as the experimental value. It is of interest that the approximate relationship

$$[8] \quad [A]_{\frac{1}{2}} = k_\infty / k_1$$

for the half pressure leads to a value of 6.78×10^3 mm.

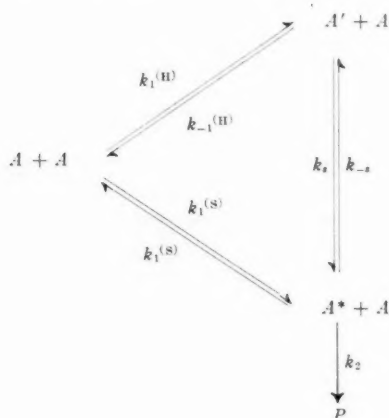
Slater's curve is of the same shape as Kassel's, but is displaced to the right as shown in Fig. 3. The predicted half pressure is 6.3×10^4 mm, which is significantly larger than the observed value.

DISCUSSION

The main conclusion of the present work is that the Kassel treatment with s equal to 2 leads to satisfactory rates over the entire pressure range, and to a reliable estimate of the half pressure. The Slater expression, however, leads to rates that are significantly too low except in the high pressure region, and to too high a value for the half pressure.*

A similar conclusion has also been reached in the case of hydrogen peroxide (3) and other small molecules (4). Since a theoretical discussion of this problem is to be presented elsewhere (4) it will suffice at the present stage to note that in the case of small molecules there appears to be flow of energy between the normal modes, as envisaged by the HKRR theories but not by Slater's theory. Our view is that Slater is right in regarding reaction as occurring when a critical co-ordinate becomes sufficiently extended, but may be in error in prohibiting flow of energy between the modes.

A scheme of reactions that is consistent with this view is



Here a distinction has been made between the two types of energized molecules, represented by A' and A^* . The A^* molecules are those that are energized in the Slater sense; they contain ϵ^* or more of energy and have it distributed between the modes in such a way that, when the vibrations come suitably into phase, there can be a sufficient extension of the critical co-ordinate. The A' molecules are energized in the less stringent HKRR sense, the energy ϵ^* or more being simply distributed between the modes and *not* being suitably distributed for reaction to occur except by a flow of energy.

This scheme of reactions leads to Slater's expression for the high-pressure rate, and in general to the HKRR formula [4] at low pressures. If there is no flow, i.e. if $k_s = k_{-s} = 0$, Slater's theory will be correct at all pressures, but otherwise the HKRR formula will apply at least over a certain range.

Further implications of the mechanism, together with a discussion of other reactions, will be discussed elsewhere (4).

*It is worth mentioning that the treatment given involves the assumption that deactivation occurs on every collision. If this is not the case the Slater and Kassel rates of energization are correspondingly reduced. The conclusion that Slater's rate of energization is too low is then true a fortiori, Kassel's rates with $s = 2$ would then be too low, but agreement might be obtained with s equal to 3 or 4.

REFERENCES

1. JOHNSTON, H. S. *J. Chem. Phys.* **19**, 663 (1951).
2. TROTMAN-DICKENSON, A. F. *Gas kinetics*. Butterworth Scientific Publications, London, 1955. p. 72.
3. GILL, E. K. and LAIDLER, K. J. To be published.
4. LAIDLER, K. J. and GILL, E. K. To be published.
5. SLATER, N. B. *Proc. Cambridge Phil. Soc.* **35**, 56 (1939).
6. SLATER, N. B. *Proc. Roy. Soc. A*, **194**, 112 (1948).
7. SLATER, N. B. *Trans. Roy. Soc. London, A*, **246**, 57 (1953).
8. SLATER, N. B. *Proc. Roy. Soc. A*, **218**, 224 (1953).
9. SLATER, N. B. *Proc. Cambridge Phil. Soc.* **50**, 33 (1954).
10. SLATER, N. B. *Proc. Leeds Phil. Lit. Soc. Sci. Sect.* **4**, 259, 268 (1955).
11. SLATER, N. B. *Proc. Roy. Soc. Edinburgh, A*, **44**, 161 (1955).
12. EYRING, H. *J. Chem. Phys.* **3**, 107 (1935).
13. GLASSTONE, S., LAIDLER, K. J., and EYRING, H. *The theory of rate processes*. McGraw-Hill Book Co., Inc., New York, 1941. p. 286.
14. HINSHELWOOD, C. N. *Proc. Roy. Soc. A*, **113**, 230 (1927).
15. KASSEL, L. S. *J. Phys. Chem.* **32**, 225 (1928).
16. KASSEL, L. S. *Kinetics of homogeneous gas reactions*. Reinhold Publishing Corp., New York, 1932. Chap. 5.
17. RICE, O. K. and RAMSPERGER, H. C. *J. Am. Chem. Soc.* **49**, 1617 (1927).
18. RICE, O. K. and RAMSPERGER, H. C. *J. Am. Chem. Soc.* **50**, 617 (1928).
19. STEARN, A. E. and EYRING, H. *J. Chem. Phys.* **3**, 778 (1935).
20. ROSENTHAL, J. E. *J. Chem. Phys.* **5**, 465 (1937).
21. BARKER, E. F. *Phys. Rev.* **41**, 369 (1932).

APPENDIX

Vibrational Analysis

The theory of vibrations in asymmetric linear triatomic molecules, and of N_2O in particular, has been discussed by Rosenthal (20). The potential and kinetic energy functions and molecular parameters employed in that paper, along with the calculated force constants, have been used in the present investigation to compute the amplitude factors and other quantities required for Slater's treatment of unimolecular reactions.

The vibrational modes were shown above in Fig. 2. The mutual displacement of the nitrogen atoms is denoted by w , while x and y are the components of the displacement of the oxygen atom relative to the center of the two nitrogen atoms; x is the displacement along the axis and y that perpendicular to it.

The most general quadratic potential function consistent with geometrical symmetry may be written in terms of four force constants:

$$[9] \quad V = \frac{1}{2}(Ax^2 + Bw^2 + Cy^2 + 2Dxw).$$

If q_{NN} and q_{NO} denote the N-N and N-O distances we may define q and α by

$$[10] \quad q \equiv q_{NN} + q_{NO},$$

$$[11] \quad \alpha \equiv q_{NN}/(2q_{NO} + q_{NN}),$$

and

$$[12] \quad \mu \equiv M/(M + 2m),$$

where M and m are the masses of the oxygen and nitrogen atoms, respectively. The kinetic energy is then

$$[13] \quad T = \frac{1}{2}m\{2\mu\dot{x}^2 + \frac{1}{2}\dot{w}^2 + 2\alpha^2\dot{y}^2[1 + (\alpha^2/\mu)]^{-1}\}.$$

Using the definitions

$$[14] \quad E \equiv 2\mu,$$

$$[15] \quad F \equiv \frac{1}{2},$$

$$[16] \quad G \equiv 2\alpha^2[1 + (\alpha^2/\mu)]^{-1},$$

the secular determinant is

$$[17] \quad \begin{vmatrix} A - mE\lambda & D & 0 \\ D & B - mF\lambda & 0 \\ 0 & 0 & C - mG\lambda \end{vmatrix} = 0.$$

The observed frequencies are (21)

$$\nu_1 = 1288.7 \text{ cm}^{-1},$$

$$\nu_2 = 588.3 \text{ cm}^{-1},$$

$$\nu_3 = 2237.9 \text{ cm}^{-1},$$

and the values derived by Rosenthal (20) are:

$$\lambda_1 = 58.94 \times 10^{26}$$

$$\lambda_3 = 1777.0 \times 10^{26}$$

$$A = 14.72 \times 10^5 \text{ dynes cm}^{-1},$$

$$B = 17.20 \times 10^5 \text{ dynes cm}^{-1},$$

$$D = -7.08 \times 10^5 \text{ dynes cm}^{-1}.$$

By the use of the secular determinant [17] it is then found that

$$\text{for } \nu_1, \quad x:w:y = (B - mF\lambda_1) : -D : 0, \\ = 1.00 : 0.429 : 0;$$

$$\text{for } \nu_2, \quad x:w:y = 0 : 0 : (C - mG\lambda_2), \\ = 0 : 0 : \text{constant};$$

$$\text{for } \nu_3, \quad x:w:y = D : -(A - mE\lambda_3) : 0, \\ = -0.857 : 1.00 : 0.$$

In the application of Slater's method employed above, the critical co-ordinate was taken as the distance between the center of mass of the N-N system and the O atom. The variation p in this co-ordinate is equal to x , and the amplitude factor α_i is given by

$$[18] \quad \alpha_i = \gamma_{xi} = x_i / \sqrt{V_{xi}}.$$

The calculated α 's were shown in Table I above, which also gives the corresponding μ 's.

The rest of the calculation is explained in the main body of the paper.

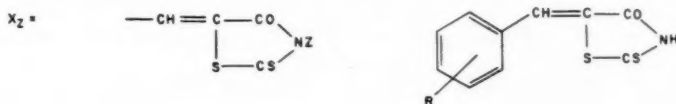
THE CONDENSATION OF RHODANINE WITH AROMATIC DIALDEHYDES AND SOME RELATED COMPOUNDS¹

FREDERICK J. ALLAN,² G. GRAHAM ALLAN,³ AND J. B. THOMSON

ABSTRACT

The condensation of rhodanine and its 3-ethyl and 3-phenyl derivatives with terephthalaldehyde, pyridine-2,6-dicarboxaldehyde, and phthalaldehyde has been investigated. Twenty-nine 5-arylidene-rhodanines containing an electrophilic substituent in the aromatic ring have been prepared.

Rhodanine condenses readily with a variety of aliphatic (1, 2, 3, 4), aromatic (5, 6), and heterocyclic (7, 8) aldehydes. The analogous reaction with ketones has been less extensively investigated (9, 10). Very few examples of rhodanine-diketone interaction have been described (11, 12, 13, 14, 15, 16) and we have been unable to find in the literature any reference to the condensation of rhodanine with dialdehydes. Our interest in rhodanine-dialdehyde adducts was actuated by the fungicidal and mildew-proofing properties of the 5-substituted rhodanines (I) in general, and the 5-arylidene-rhodanines (II) in particular (5, 6). In spite of the many variants of R in (II) only two compounds in which R is electrophilic have been evaluated as fungicides (5). The location of the substituent diminished or increased the fungitoxicity of (II), suggesting evaluation of electron distribution as a rationale for structure and activity. With a view to preparing further examples of this type of compound for testing we have examined the condensation of some aromatic dialdehydes with rhodanine derivatives.



in X_H (Z = H), X_Et (Z = C_2H_5), X_Ph (Z = C_6H_5).

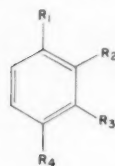
Termolecular reaction of rhodanine and the 3-ethyl and 3-phenyl derivatives (two molecular proportions) with terephthalaldehyde (IIIa) or pyridine-2,6-dicarboxaldehyde (IVa) (one molecular proportion) proceeds with great facility to yield the diadducts (IIIb), (IIIc), (IIId), (IVb), (IVc), and (IVd) respectively, which separated from the reaction mixture in an almost pure state. The aldehyde-rhodanine derivatives were prepared using ammonia - ammonium chloride (17), acetic acid - sodium acetate (19), or acetic acid - acetic anhydride - sodium acetate (7) as condensing agents. No crystalline adducts were obtained from the reaction of phthalaldehyde with either rhodanine, 3-ethyl-, or 3-phenyl-rhodanine using these reagents or with 3-ethylrhodanine under the conditions used to condense phthalaldehyde with malonic ester (18). Condensation of equimolecular proportions of 3-ethyl- or 3-phenyl-rhodanine (but not rhodanine itself) with the dialdehydes (IIIa) and (IVa) gave readily separable mixtures of the appropriate diadducts

¹Manuscript received June 5, 1958.

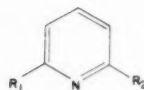
Contribution from the Department of Chemistry, Paisley Technical College, Paisley, Scotland.

²To whom enquiries should be addressed.

³Present address: Electrochemicals Department, E. I. duPont de Nemours & Co., Inc., Wilmington, Del., U.S.A.



(III)



(IV)

III

- a.* $R_1 = R_4 = \text{CHO}; R_2 = R_3 = \text{H}$
b. $R_1 = R_4 = \text{X}_{\text{H}}; R_2 = R_3 = \text{H}$
c. $R_1 = R_4 = \text{X}_{\text{Et}}; R_2 = R_3 = \text{H}$
d. $R_1 = R_4 = \text{X}_{\text{Ph}}; R_2 = R_3 = \text{H}$
e. $R_1 = \text{CHO}; R_2 = R_3 = \text{H}; R_4 = \text{X}_{\text{Et}}$
f. $R_1 = \text{CHO}; R_2 = R_3 = \text{H}; R_4 = \text{X}_{\text{Ph}}$
g. $R_1 = \text{CH:NOH}; R_2 = R_3 = \text{H}; R_4 = \text{X}_{\text{Ph}}$
h. $R_1 = \text{X}_{\text{H}}; R_2 = \text{NO}_2; R_3 = R_4 = \text{H}$
i. $R_1 = \text{X}_{\text{Et}}; R_2 = \text{NO}_2; R_3 = R_4 = \text{H}$
j. $R_1 = \text{X}_{\text{Ph}}; R_2 = \text{NO}_2; R_3 = R_4 = \text{H}$
k. $R_1 = \text{X}_{\text{H}}; R_3 = \text{NO}_2; R_2 = R_4 = \text{H}$

- l.* $R_1 = \text{X}_{\text{Et}}; R_3 = \text{NO}_2; R_2 = R_4 = \text{H}$
m. $R_1 = \text{X}_{\text{Ph}}; R_3 = \text{NO}_2; R_2 = R_4 = \text{H}$
n. $R_1 = \text{X}_{\text{H}}; R_4 = \text{NO}_2; R_2 = R_3 = \text{H}$
o. $R_1 = \text{X}_{\text{Et}}; R_4 = \text{NO}_2; R_2 = R_3 = \text{H}$
p. $R_1 = \text{X}_{\text{Ph}}; R_4 = \text{NO}_2; R_2 = R_3 = \text{H}$
q. $R_1 = \text{X}_{\text{H}}; R_2 = \text{CO}_2\text{H}; R_3 = R_4 = \text{H}$
r. $R_1 = \text{X}_{\text{Et}}; R_2 = \text{CO}_2\text{H}; R_3 = R_4 = \text{H}$
s. $R_1 = \text{X}_{\text{Ph}}; R_2 = \text{CO}_2\text{H}; R_3 = R_4 = \text{H}$
t. $R_1 = \text{X}_{\text{H}}; R_4 = \text{CO}_2\text{H}; R_2 = R_3 = \text{H}$
u. $R_1 = \text{X}_{\text{Et}}; R_4 = \text{CO}_2\text{H}; R_2 = R_3 = \text{H}$
v. $R_1 = \text{X}_{\text{Ph}}; R_4 = \text{CO}_2\text{H}; R_2 = R_3 = \text{H}$

IV

- a.* $R_1 = R_2 = \text{CHO}$
b. $R_1 = R_2 = \text{X}_{\text{H}}$
c. $R_1 = R_2 = \text{X}_{\text{Et}}$
d. $R_1 = R_2 = \text{X}_{\text{Ph}}$
e. $R_1 = \text{CHO}; R_2 = \text{X}_{\text{Et}}$
f. $R_1 = \text{CHO}; R_2 = \text{X}_{\text{Ph}}$

described above and the related monoadducts (IIIe), (IIIf), (IVe), and (IVf). The retention of a free formyl group under the conditions of condensation is evidenced by analysis and the formation of an oxime (IIIg).

Concurrently with this study we have prepared for fungicidal and antibacterial evaluation* fifteen 5-arylidene-rhodanines (II) containing an electrophilic substituent in the benzenoid moiety and comprising two groups. The first group consists of the adducts (IIIh) to (IIIp) inclusive, containing the toxiphoric nitro group, which were synthesized by the condensation of rhodanine, its 3-ethyl and 3-phenyl homologues with 2-, 3-, and 4-nitrobenzaldehyde. The second group of adducts, (IIIq) to (IIIv) inclusive, was derived from the condensation of rhodanine and its congeners with phthalaldehydic and terephthalaldehydic acid; analogous derivatives of which have recently received attention as bactericidal agents (20, 21).

EXPERIMENTAL†

1,4-Phenylene-di-(5-methylenerrhodanine) (IIIb)

A solution of terephthalaldehyde (1.34 g, 0.01 mole) and rhodanine (2.66 g, 0.02 mole) in ethanol (20 ml) and concentrated ammonium hydroxide (7 ml, d., 0.88) was heated on the steam bath. A solution of ammonium chloride (7 g) in hot water (10 ml) was added and heating continued for 1 hour when orange needles had separated. Recrystallization from dimethylformamide gave the diadduct IIIb as fine orange needles (2.8 g, yield 77%) which did not melt below 360°. Calc. for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2\text{S}_4$: C, 46.08; H, 2.2; N, 7.68; S, 35.25. Found: C, 45.81; H, 1.95; N, 7.31; S, 35.00%.

*Details of which we hope to publish later elsewhere.

†Melting points have been corrected.

| Compound* | Structure | Crystalline form† | M.p., °C | Yield % | Formula | Carbon, % | | Hydrogen, % | |
|------------------------------------------------------------|-----------|-----------------------------------------------|-------------------|---------|------------------------------------------------------------------------------|-----------|-------|-------------|-------|
| | | | | | | Calc. | Found | Calc. | Found |
| 1,4-Phenylene-di-(3-phenyl-5-methylenethiodaniline) | III d | Fine orange needles ^a | >360 | 86 | C ₂₁ H ₁₈ N ₂ O ₂ S ₂ | 60.39 | 60.34 | 3.12 | 3.27 |
| 2,6-(1-Azaphenylene)-di-(3-ethyl-5-methylenethiodaniline)‡ | IV c | Fine yellow needles ^b | 228-229 | 93 | C ₂₁ H ₁₈ N ₂ O ₂ S ₂ | 48.39 | 48.52 | 3.58 | 3.68 |
| 2,6-(1-Azaphenylene)-di-(3-phenyl-5-methylenethiodaniline) | IV d | Fine orange needles ^a | 335-336 (decomp.) | 87 | C ₂₁ H ₁₈ N ₂ O ₂ S ₂ | 57.97 | 57.63 | 2.92 | 3.01 |
| 5-(2-Nitrobenzylidene)rhodanine‡ | III h | Yellow needles ^c | 204-205 | 71 | C ₁₆ H ₁₀ N ₂ O ₂ S | 45.09 | 45.31 | 2.27 | 2.13 |
| 3-Ethyl-5-(2-nitrobenzylidene)rhodanine | III i | Orange plates ^d | 157-158 | 85 | C ₁₈ H ₁₄ N ₂ O ₂ S | 48.96 | 48.73 | 3.42 | 3.21 |
| 3-Phenyl-5-(2-nitrobenzylidene)rhodanine§ | III j | Orange plates ^d | 245-246 | 45 | C ₂₁ H ₁₈ N ₂ O ₂ S | 56.12 | 55.98 | 2.94 | 3.05 |
| 5-(3-Nitrobenzylidene)rhodanine | III k | Bright yellow needles ^a | 204-205 | 60 | C ₁₈ H ₁₄ N ₂ O ₂ S | 45.09 | 44.85 | 2.27 | 2.01 |
| 3-Ethyl-5-(3-nitrobenzylidene)rhodanine¶ | III l | Golden-yellow blades ^a | 194-195 | 58 | C ₁₈ H ₁₄ N ₂ O ₂ S | 48.96 | 48.07 | 3.42 | 3.28 |
| 3-Phenyl-5-(3-nitrobenzylidene)rhodanine** | III m | Orange platelets ^a | 245-246 | 48 | C ₂₁ H ₁₈ N ₂ O ₂ S | 56.12 | 56.41 | 2.94 | 2.72 |
| 5-(4-Nitrobenzylidene)rhodanine†† | III n | Orange-yellow needles ^d | 273-274 | 90 | C ₁₈ H ₁₄ N ₂ O ₂ S | 45.09 | 44.76 | 2.27 | 2.41 |
| 3-Ethyl-5-(4-nitrobenzylidene)rhodanine‡‡ | III o | Orange-yellow prismatic needles ^d | 232-233 | 85 | C ₁₈ H ₁₄ N ₂ O ₂ S | 48.96 | 48.88 | 3.42 | 3.19 |
| 3-Phenyl-5-(4-nitrobenzylidene)rhodanine§§ | III p | Yellow needles ^a | 273-274 | 96 | C ₂₁ H ₁₈ N ₂ O ₂ S | 56.12 | 55.88 | 2.94 | 2.69 |
| 3-Ethyl-5-(2-carboxybenzylidene)rhodanine | III r | Golden-yellow rectangular plates ^c | 185-187 | 52 | C ₁₈ H ₁₂ N ₂ O ₄ S | 53.22 | 52.96 | 3.78 | 3.82 |
| 5-(4-Carboxybenzylidene)rhodanine | III s | Yellow-orange felted needles ^d | 225-226 | 70 | C ₁₈ H ₁₂ N ₂ O ₄ S | 59.80 | 59.67 | 3.25 | 3.17 |
| 3-Phenyl-5-(2-carboxybenzylidene)rhodanine | III t | Yellow-orange prismatic needles ^b | 307-308 (decomp.) | 80 | C ₂₁ H ₁₆ N ₂ O ₄ S | 49.79 | 49.61 | 2.65 | 2.53 |
| 3-Ethyl-5-(4-carboxybenzylidene)rhodanine | III u | Golden-yellow needles ^b | 290-291 | 79 | C ₂₁ H ₁₆ N ₂ O ₄ S | 53.22 | 52.99 | 3.78 | 3.52 |
| 3-Phenyl-5-(4-carboxybenzylidene)rhodanine | III v | Orange-yellow prisms ^a | 307-308 | 85 | C ₂₁ H ₁₆ N ₂ O ₄ S | 59.80 | 59.63 | 3.25 | 3.31 |

*The 17 compounds appearing in this table were similarly prepared.

†Crystallization solvents: ^adimethylformamide, ^bacetic acid, ^cmethanol, ^dacetone-methanol, ^ebenzene-methanol.

‡Bondzynski (22) gives m.p. 188-189° for this compound prepared by the condensation of 2-nitrobenzaldehyde with rhodanine in ethanol containing sulphuric acid.

§Andresch and Zipser (23) give m.p. 238° for this compound prepared by the same method.

||Bargellini (24) gives m.p. 245-255° for this compound prepared by the condensation of 3-nitrobenzaldehyde with rhodanine in ethanol containing sulphuric acid.

**Andresch and Zipser (25) give m.p. 188° for this compound prepared by the same method.

††Bondzynski (22) gives m.p. 250-252° (decomp.) for this compound prepared by the condensation of 4-nitrobenzaldehyde with rhodanine in ethanol containing sulphuric acid.

‡‡Andresch and Zipser (25) give m.p. 240° (decomp.) for this compound prepared by the same method.

§§Nitrogen analysis: Calc., 9.96; found, 9.71%.

|||Nitrogen analysis: Calc., 8.11; found, 7.93%.

*2,6-(1-Azaphenylene)-di-(5-methylenerrhodanine) (IVb)**

2,6-(1-Azaphenylene)-di-(5-methylenerrhodanine) (IVb), fine bright yellow needles (100 mg, yield 52%), from dimethylformamide, which did not melt below 360°. Calc. for $C_{13}H_7N_3O_2S_4$: C, 42.82; H, 1.94; N, 11.53. Found: C, 43.14; H, 1.94; N, 11.63%.

*5-(2-Carboxybenzylidene)rhodanine (IIIq)**

5-(2-Carboxybenzylidene)rhodanine (IIIq), clusters of bright yellow needles (1.1 g, yield 42%) from aqueous ethanol, m.p. 268–270° with decomp. Calc. for $C_{11}H_7NO_3S_2$: C, 49.79; H, 2.65. Found: C, 49.58; H, 2.78%. Dijkman and Newbold (19) give m.p. 265–266° for this compound prepared by the condensation of phthaldehydic acid with rhodanine in acetic acid containing sodium acetate.

1,4-Phenylene-di-(3-ethyl-5-methylenerrhodanine) (IIIc)

A mixture of terephthaldehyde (0.67 g, 0.005 mole), 3-ethylrhodanine (1.62 g, 0.01 mole), and freshly fused sodium acetate (3 g) in acetic acid (50 ml), to which acetic anhydride (1 ml) had been added, was refluxed for 1 hour during which time orange needles separated. The mixture was allowed to cool and the product collected. Recrystallization from acetic acid gave the diadduct IIIc as long prismatic orange needles (1.5 g, yield 71%) m.p. 295–296°. Calc. for $C_{18}H_{16}N_2O_2S_4$: C, 51.35; H, 3.83. Found: C, 51.42; H, 3.94%.

3-Ethyl-5-(4-formylbenzylidene)rhodanine (IIIe)

A mixture of terephthaldehyde (1.34 g, 0.01 mole), 3-ethylrhodanine (1.62 g, 0.01 mole), and freshly fused sodium acetate (3 g) in acetic acid (50 ml), to which acetic anhydride (1 ml) had been added, was refluxed for 1 hour when crystals had separated. The hot reaction mixture was filtered and the diadduct (IIIc) (1.25 g) removed. The filtrate was diluted with water (100 ml) and the yellow precipitate collected and washed with hot water. Crystallization from acetone-methanol gave 3-ethyl-5-(4-formylbenzylidene)rhodanine (550 mg, yield 20%) as orange-yellow plates, m.p. 171–172°. Calc. for $C_{13}H_{11}NO_2S_2$: C, 56.29; H, 4.0. Found: C, 56.48; H, 4.06%.

3-Phenyl-5-(4-formylbenzylidene)rhodanine (IIIff)†

3-Phenyl-5-(4-formylbenzylidene)rhodanine (IIIff), yellow needles (1.71 g, yield 53%) from benzene-ethanol, m.p. 233–234°. Calc. for $C_{17}H_{11}NO_2S_2$: C, 62.82; H, 3.41. Found: C, 62.71; H, 3.45%. The related *oxime* (IIIg) was prepared in pyridine-ethanol solution (26) and crystallized from benzene-ethanol as yellow needles, m.p. 276–278°. Calc. for $C_{17}H_{12}N_2O_2S_2$: C, 59.96; H, 3.55. Found: C, 59.77; H, 3.69%.

3-Ethyl-5-[2-(6-formyl)pyridylmethylene]rhodanine (IVe)†

3-Ethyl-5-[2-(6-formyl)pyridylmethylene]rhodanine (IVe), yellow prismatic needles (500 mg, yield 18%) from aqueous methanol, m.p. 191–192°. Calc. for $C_{12}H_{10}N_2O_2S_2$: C, 51.78; H, 3.62. Found: C, 51.53; H, 3.45%.

3-Phenyl-5-[2-(6-formyl)pyridylmethylene]rhodanine (IVff)†

3-Phenyl-5-[2-(6-formyl)pyridylmethylene]rhodanine (IVff), clusters of yellow prismatic needles (1.98 g, yield 60%) from methanol, m.p. 248–250°. Calc. for $C_{16}H_{10}N_2O_2S_2$: C, 58.88; H, 3.09. Found: C, 58.52; H, 3.01%.

*The compounds designated by * were similarly prepared.

†The compounds designated by † were similarly obtained.

REFERENCES

1. NENCKI, M. Ber. **17**, 2277 (1884).
2. GRANACHER, C., GERO, M., OFNER, A., KLOPFENSTEIN, A., and SCHLATTER, E. Helv. Chim. Acta, **6**, 458 (1923).
3. ANDREASCH, R. Monatsh. **39**, 419 (1918).
4. ANDREASCH, R. Monatsh. **49**, 122 (1928).
5. BROWN, F. C., BRADSHER, C. K., and BOND, S. M. Ind. Eng. Chem. **45**, 1030 (1953).
6. BROWN, F. C., BRADSHER, C. K., BOND, S. M., and POTTER, M. J. Am. Chem. Soc. **73**, 2357 (1951) and previous references therein cited.
7. ALLAN, F. J., ALLAN, G. G., and THOMSON, J. B. J. Org. Chem. **23**, 112 (1958) and previous references therein cited.
8. NEU, R. Ber. **90**, 2638 (1957).
9. BROWN, F. C., BRADSHER, C. K., MCCALLUM, S., and POTTER, M. J. Org. Chem. **15**, 174 (1950).
10. ALLAN, G. G., MACLEAN, D., and NEWBOLD, G. T. J. Chem. Soc. 5053 (1952).
11. BUTSCHER, E. Monatsh. **32**, 9 (1911).
12. GRANACHER, C., REIS, H., and POOL, E. Helv. Chim. Acta, **5**, 382 (1922).
13. GRANACHER, C. and MAHAL, A. Helv. Chim. Acta, **6**, 467 (1923).
14. JONES, H. A. and HANN, R. M. J. Am. Chem. Soc. **50**, 2491 (1928).
15. JONES, R. V. and HENZE, H. R. J. Am. Chem. Soc. **64**, 1669 (1942).
16. KNOTT, E. B. To Kodak Ltd., Brit. Patent No. 753,648, July 25, 1956.
17. GIRARD, M. Ann. chim. **16**, 326 (1941).
18. WILEY, R. H. and HOBSON, P. H. J. Am. Chem. Soc. **71**, 2429 (1949).
19. DIJKSMAN, D. J. and NEWBOLD, G. T. J. Chem. Soc. 1213 (1951).
20. WHEELER, D. D. and YOUNG, D. C. To Dow Chemical Co., U.S. Patent Nos. 2,802,830 to 2,802,837, Aug. 13, 1957; 2,811,535, 2,811,536, Oct. 29, 1957; 2,814,627, Nov. 26, 1957; 2,817,668, Dec. 24, 1957; 2,819,286, 2,819,287, Jan. 7, 1958.
21. KAWARA, K. and KOBAYASHI, H. To Dai Nippon Drug Mfg. Co., Japan. Patent No. 2,838, April 16, 1956. Chem. Abstr. **51**, 9693 (1957).
22. BONDZYSKI, S. Monatsh. **8**, 349 (1887).
23. ANDREASCH, R. and ZIPSER, A. Monatsh. **24**, 499 (1903).
24. BARGELLINI, G. Gazz. chim. ital. **36**, II, 129 (1906).
25. ANDREASCH, R. and ZIPSER, A. Monatsh. **25**, 176 (1904).
26. SHRINER, R. L. and FUSON, R. C. Identification of organic compounds. 2nd ed. John Wiley & Sons, Inc., New York. 1946. p. 167.

LIGHT-SCATTERING STUDIES ON ALUMINUM DISTEARATE¹

A. E. LEGER, J. C. HYDE, AND H. SHEFFER

ABSTRACT

A light-scattering study of aluminum distearate in dilute benzene solution suggests that it is a linear molecule of random coil shape. This is further substantiated by intrinsic viscosity - molecular weight data, the constancy of the ratio of the molecular weight to the square of the radius of gyration (R_g), the value of Φ in Flory's intrinsic viscosity - molecular weight relationship, and the close agreement between the theoretical and experimental results found for the unit length of the polymer chain. This average unit length has been calculated to be 4.46 Å.

INTRODUCTION

The fundamental structure of aluminum soaps remains rather obscure, although most authors (1, 2, 3, 4, 5, 6, 7, 8) agree that these substances dispersed in organic solvents are high polymers, the monomeric unit being the basic aluminum disoap, e.g. aluminum hydroxydistearate. Opinions differ, however, as to the nature of the chemical bonding between the monomeric units. McGee (6) and Gray and Alexander (5) have proposed an alternation of covalent and co-ordination bonds between the aluminum atom and oxygen atom of the hydroxyl radical to form the polymer chain. McBain (2) favors an association of the molecules into micelles, while McRoberts and Schulman (3) attribute the weak type of bonding exhibited by these molecules to hydrogen bonding. Recently the present authors (8) and Bauer *et al.* (7) gave evidence in favor of a structure similar to that proposed by Gray and Alexander, but with the carboxylate group also acting as a bridge between two aluminum atoms. These co-ordination bridge structures could easily be broken and could account for the changes in physical properties of solutions or gels on dilution, peptization, or on aging.

It has always been recognized that aluminum soap solutions are relatively unstable and deteriorate with time, with a gradual lowering of the molecular weight of the polymer. This instability has not as yet been fully explained but the breakdown is accelerated by moisture and in general by traces of acid or other polar compounds. The rate of change depends on the concentration, the more concentrated solutions being relatively more stable. A complete explanation of the physicochemical properties of aluminum soap solutions is impossible without a detailed knowledge of the structure of the soap molecule. It was considered important to obtain more data on molecular weight and viscosity characteristics of aluminum stearate solutions and deduce from these, if possible, the average size and shape of the molecules. It was recognized that interpretation of the results would be hampered by the instability of the polymer, so the experimental techniques employed were designed to diminish as much as possible its effect on the experimental data. Another limitation of the interpretation of the data lies in our lack of knowledge of molecular weight distribution characteristics and of any method of fractionation for this polymer.

Aluminum distearate swells in cold benzene and complete solution can be effected only by heating the mixture for some time. It would appear that the soap is a complex, probably cross-linked, polymer with relatively weak bonds. Prolonged heating causes the breakage of some of these bonds, resulting in a solution of polymer whose average molecular weight depends on the concentration.

¹Manuscript received July 9, 1958.

Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada.

Issued as D.R.C.L. Report No. 285.

If viscosity data are obtained for a series of solutions of differing concentration, made up by refluxing under standard conditions, a curve of the general shape OAB, as shown in Fig. 1, results. For a "starting" or refluxed solution of concentration 0.4%, point B is obtained. On dilution of this solution to 0.2% the reduced viscosity does not revert to point A but rather to point E (4), and by obtaining further points on the line BEC an intrinsic viscosity which is characteristic of the polymer in the 0.4% solution can be extrapolated. Similarly, dilution of the "starting" 0.2% solution gives the line AD and a lower intrinsic viscosity. Thus one can obtain characteristic intrinsic viscosities and corresponding average molecular weights for the polymers in the "starting" solutions. Viscosity and osmotic pressure data obtained in this manner were reported previously (4) and this paper extends the work to include light-scattering information.

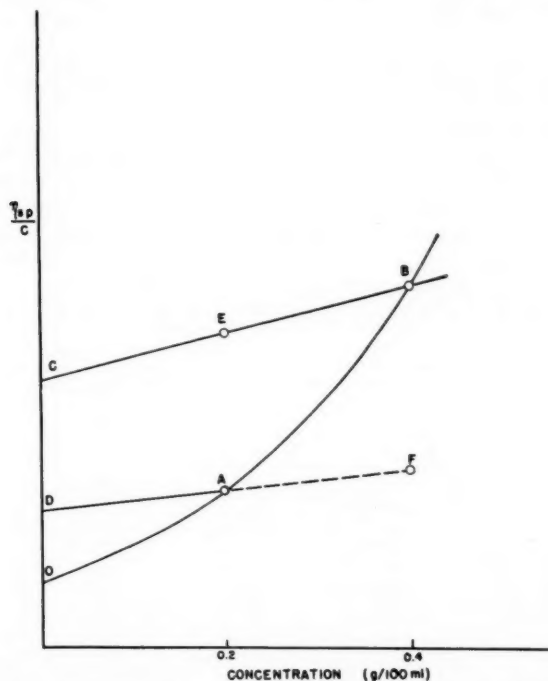


FIG. 1. A graphical representation of aluminum soap solution viscosity with changing concentration.

The fact that on dilution of solution B point E rather than A was obtained is an indication that the polymer is not merely an association colloid. Two other pieces of supporting evidence may be cited. One is that by melting and slowly resolidifying the soap under vacuum, material of much higher molecular weight is obtained (4) indicating that more polymer bonds are formed in the solid by this process than by association in solution. The other is concerned with the concentration of a dilute to a more concentrated one by evaporation of solution. On concentration of a 0.2% solution (point A) to 0.4%, point F on Fig. 1 is obtained rather than point B, which would be expected if the polymer were associating to larger micelles as the concentration is increased. This latter point was

checked by light-scattering technique and it was found that solution *F* contained polymer of molecular weight within 10% of that of solution *A*, while solution *B* contained polymer of about five times the average molecular weight of polymer in solution *A*.

EXPERIMENTAL

Reagents

The aluminum distearate used in this investigation was prepared by the method described previously (4) and extracted with dry acetone in a Soxhlet to remove free fatty acid. Solutions were prepared by refluxing the soap in specially dried benzene for 1½ hours under anhydrous conditions. A small portion of the benzene was distilled at the start of the refluxing period to remove any residual moisture from the soap, solvent, and glassware.

Viscosity

Viscosity measurements were made at $30^\circ \pm 0.01^\circ \text{C}$ using Ostwald viscometers with a benzene flowtime of about 100 seconds, and the data were corrected for kinetic energy.

Light-Scattering Measurements

The apparatus used for the light-scattering measurements has been described previously (9). The cell in cross section is half of a regular dodecagon so that it is possible to measure scattering at 90° and at two pairs of angles about 90° (33° and 147° , 60° and 120°). The appropriate correction for reflection at the exit face (10) was made. The wavelength used was 5461 Å, obtained from a mercury-vapor lamp (General Electric AH-4) with suitable filters. Reduced intensities were plotted by the Zimm method, extrapolating the data to zero angle and infinite dilution. A typical Zimm plot of the experimental data is given in Fig. 2.

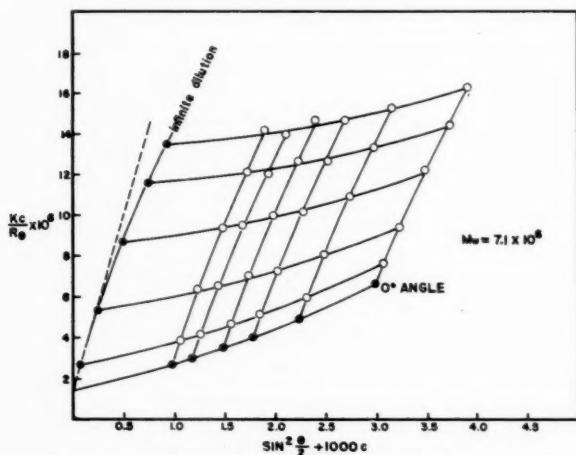


FIG. 2. A typical Zimm plot of experimental data obtained for aluminum distearate in benzene solution.

All measurements were made on aluminum distearate-benzene solutions previously cleared of dust particles by centrifuging at about 25,000 *g* for a few hours prior to use. A large number of "starting" solutions were prepared and the dilutions and measurements were made as fast as possible, the total time taken for each series being about 30 minutes.

RESULTS

A. Molecular Shape

The correlation of experimental data with theory is complicated by the lack of knowledge of the molecular weight distribution and by the possibility of branching of the polymer. However, it is possible to determine the radius of gyration (R_g) from the ratio of initial slope to the intercept in the Zimm plot, and the weight-average molecular weight from the reciprocal of the intercept of the infinite dilution curve. The use of the Zimm method obviates the necessity of making assumptions of the particle shape to obtain either value. The radius of gyration (R_g) and the weight-average molecular weight (M_w) are given in Table I for 21 different "starting" solutions of aluminum distearate. The ratio of the molecular weight M_w to the radius of gyration (M/R_g), to the square of the radius of gyration (M/R_g^2), and to the cube of the radius of gyration (M/R_g^3) are also given. It has previously been found (11, p. 211) that M/R_g is constant for spherical, $M/(R_g)^2$ for random-coiled, and $M/(R_g)^3$ for rod-shaped particles. As can be seen from Table I the ratio of M/R_g^2 has the greatest constancy. In making these calculations it is recognized that the absolute value of these ratios are in error as the molecular weight used is a weight average and R_g is a "Z" average length. Since, however, the "Z" and "W" average molecular weights will not have a widely varying ratio to one another, no great error is introduced in the constancy of the molecular weight radius of gyration ratio. This is especially true in the present case where the molecular weights considered are very high.

TABLE I
VALUES OF RADIUS OF GYRATION TO MOLECULAR WEIGHT RATIOS

| $M_w \times 10^{-6}$ | $R_g \text{ \AA}$ | $M/R_g \times 10^{-2}$ | $M/(R_g)^2 \times 10^{+2}$ | $M/(R_g)^3 \times 10^{+5}$ | $(\bar{r}^2)^{\frac{1}{2}} \text{ \AA}$ |
|----------------------|-------------------|------------------------|----------------------------|----------------------------|-----------------------------------------|
| 25.8 | 2790 | 8.95 | 3.20 | 1.13 | 6840 |
| 12.9 | 2010 | 6.42 | 3.20 | 1.56 | 4920 |
| 11.5 | 1800 | 6.39 | 3.54 | 1.97 | 4400 |
| 10.9 | 1710 | 6.39 | 3.73 | 2.18 | 4200 |
| 7.35 | 1510 | 4.86 | 3.22 | 2.14 | 3690 |
| 6.50 | 1430 | 4.55 | 3.18 | 2.22 | 3500 |
| 6.45 | 1580 | 4.09 | 2.59 | 1.64 | 3870 |
| 6.45 | 1520 | 4.24 | 2.78 | 1.83 | 3730 |
| 5.72 | 1490 | 3.84 | 2.58 | 1.73 | 3660 |
| 5.10 | 1350 | 3.78 | 2.80 | 2.08 | 3320 |
| 3.96 | 1270 | 3.12 | 2.46 | 1.94 | 3120 |
| 3.82 | 1240 | 3.08 | 2.48 | 2.00 | 3030 |
| 3.74 | 1150 | 3.25 | 2.82 | 2.46 | 2830 |
| 3.68 | 1190 | 3.09 | 2.60 | 2.38 | 2910 |
| 3.39 | 1220 | 2.78 | 2.28 | 1.87 | 2990 |
| 2.58 | 1020 | 2.52 | 2.47 | 2.42 | 2500 |
| 2.34 | 910 | 2.56 | 2.81 | 3.08 | 2220 |
| 1.32 | 750 | 1.76 | 2.35 | 3.14 | 1840 |
| 1.25 | 660 | 1.90 | 2.88 | 4.37 | 1660 |

The relative constancy of the M/R_g^2 ratio is an indication that the molecules are of the random coil type. It is known that for a random coil configuration the root-mean-square end-to-end length $(\bar{r}^2)^{\frac{1}{2}}$ is equal to $R_g \sqrt{6}$. This relationship has been used to calculate the values of $(\bar{r}^2)^{\frac{1}{2}}$ given in Table I.

It is also possible to correlate the light-scattering data with theoretically derived curves for spheres, coils, and rods and to determine which of these molecular shapes most closely satisfies the experimental data. The theoretical curves were calculated from the theoretical scattering functions for spheres, rods, and random coils and fitted to the experimental data to obtain the same 0° and 90° scattering. As can be seen in Fig. 3 the

experimental values are very close to the theoretical curves for random coils. Deviations of the curves could be explained by differences in polydispersity, branching, stiffness, or extension of the coils, and at the present time it would seem impossible to distinguish between these variables (12, 13).

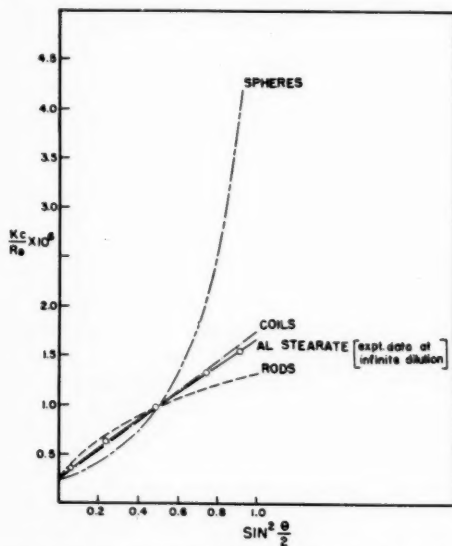


FIG. 3. A comparison of experimental data for aluminum distearate with theoretical curves for spheres, random coils, and rods.

Both the constancy of M/R_g^2 and the close agreement of the theoretical and experimental values lead to the conclusion that the molecules are indeed of the random coil type. This permits us to calculate the root-mean-square end-to-end distance as already noted and, as will be seen below, to derive some idea of the dimensions of the unit length of the molecule.

B. Viscosity - Molecular Weight Relationship

It is possible to derive some measure of the relationship between the intrinsic viscosity $[\eta]$ and the molecular weight of aluminum distearate (see Fig. 4). Although the data for extreme molecular weights introduce a curvature to the plot, for a large range of molecular weights this curve could be replaced by a straight line, within experimental error, which would correspond very closely to the theoretical value for linear molecules. This is shown by the dotted line in Fig. 4, its position having been determined by the least-squares method by neglecting the very high molecular weight and the very low viscosity values, which are less precise owing to experimental difficulties. The equation for this line is

$$[\eta] = 2.93 \times 10^{-4} M^{0.58}$$

in which the value for α in $[\eta] = KM^\alpha$ corresponds rather closely to the expected value of 0.5, the theoretical value for linear molecules such as polybutadiene.

Huggins' " k " values were calculated from the slope of the reduced viscosity-concentration curves. Its average value was 0.77, but the scatter of the experimental data

made it impossible to determine any possible molecular weight dependence. This value for k' is lower and more constant than those obtained previously (4) owing to a more precise method of measuring viscosity. In general, k' values greater than 0.5 have been accounted for by branching in well-fractionated polymer samples. Interpretation of the results in aluminum soap solutions is further complicated by the known polydispersity of the polymer and it would seem impossible at this time to separate one effect from the other.

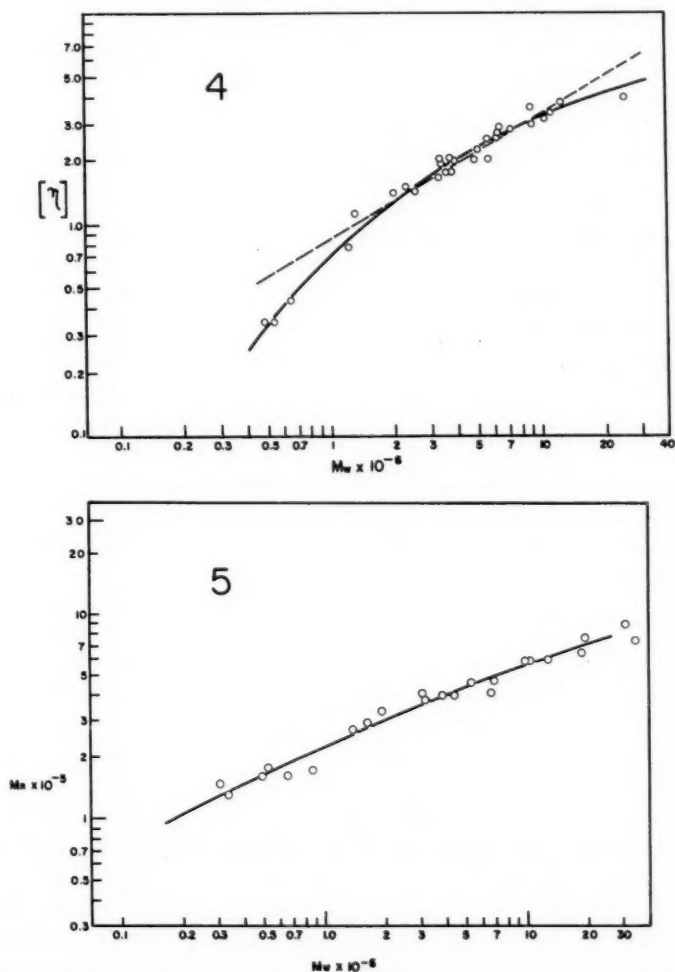


FIG. 4. Intrinsic viscosity $[\eta]$ as a function of weight-average molecular weight (M_w) of aluminum distearate in benzene solution. The dotted line was obtained by neglecting three low molecular weight points and one high molecular weight point and drawing a straight line through the remainder by the method of least squares.

FIG. 5. Number-average molecular weight (M_n) as a function of weight-average molecular weight (M_w) for aluminum distearate in benzene solution.

C. Number-Average and Weight-Average Molecular Weight Correlations

Previously published data (4) gave the relationship of number-average molecular weight (M_n) as measured by the osmotic pressure method to intrinsic viscosity.

The present study gives the weight-average molecular weight (M_w) also as a function of intrinsic viscosity. It is thus possible to correlate M_n to M_w and to indicate the polydispersity of the polymer. This relationship is shown in Fig. 5. Most of the data used in the $[\eta]$ - M_n curve were obtained for aluminum dilaurate, but since there did not seem to be any significant change in this relationship for other aluminum soaps, the same values were used for aluminum stearate. The ratio of M_w/M_n varies from about 30 for an M_w of 10^7 to about 3 for an M_w of 10^6 . This relationship emphasizes the very wide polydispersity of the aluminum soaps and will be used below to calculate unit lengths in aluminum soap polymers.

As the polymer chains are broken down to lower molecular weight units the polydispersity decreases. Evidence was obtained to show that bond breakage does not occur near the end of the chain to form monomers or other small units. For this a Fuoss-Mead osmometer was used with a "fast" membrane, and diffusion rates through the membrane were obtained for a series of polystyrene fractions of known molecular weight. Comparing the results with those obtained for aluminum stearate solutions it was ascertained that not more than traces of soap polymer were present with molecular weight below 80,000.

D. Unit Length in Aluminum Stearate Polymer

It should be possible to derive an estimate of the unit length of the polymer chain by making certain assumptions. A molecular model for aluminum disoap has been proposed by Bauer *et al.* (7) and modified by the present authors (8).

Fig. 6 gives details of this modified model. In the actual molecular configuration, it is of

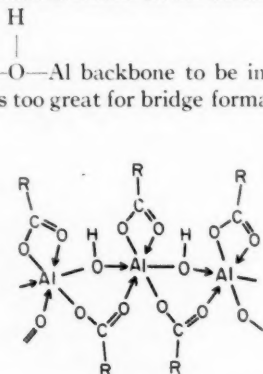


FIG. 6. Chemical formula of the aluminum soap molecule showing bridged and non-bridged carboxylate groups.

The evidence in favor of a bridge-type structure for the carboxylate group is mainly derived from experimental infrared absorption measurements. It has previously been shown (8) that in both aluminum tri- and di-soap two major absorption bands occur in the 6.1 – 6.4μ region, and that these bands can be assigned to bridged and non-bridged carboxylate groups. This experimental evidence is corroborated by viscosity and molecular weight measurements. Bauer (7) has shown that peptization studies on aluminum disoaps can also be explained by a bridge-type structure.

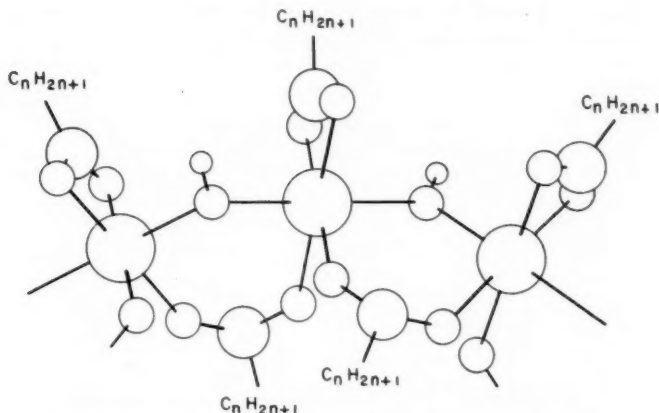


FIG. 7. Model of aluminum soap molecule showing bridged and non-bridged carboxylate groups.

The assumptions that are made in choosing this model are these:

1. The Al—O distances around the Al atoms are all equal. This assumption is probably not strictly accurate, and it is probable that the aluminum to hydroxyl bond length is greater than the aluminum—carboxylate distance, but this approximation is made to facilitate calculations in the absence of any definite value.
2. The O—O distance of a carboxylate group is taken as 2.28 Å, derived from an OCO angle of 125° and O—C bond length of 1.29 Å (14, p. 203).
3. The Al—O distance was taken as 1.92 Å, which is the sum of the covalent radii (14, p. 179). This gives a length of 2.71 Å for the O—O distance between the hydroxyl and carboxylate oxygen positions. This is higher than the 2.50 Å result found for most crystals in which aluminum—oxygen bonds are present.

The distances and angles involved in the calculation of the Al—O—Al bond angle are given in Fig. 8. The values of the Al—O—Al angle found by substituting plausible values of the O—O distance in the carboxylate group are given in Table II. These vary from a minimum of 130° to a maximum of 144°. The most probable value would probably be intermediate between all of these. For calculation purposes 135° was taken as the angle

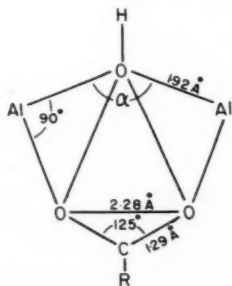


FIG. 8. Diagram of a portion of the aluminum soap molecule drawn through the Al—O—Al plane and showing its principal dimensions.

Al—O—Al. This value could be compared to 130°–160° proposed for the Si—O—Si angle in polysiloxanes (15).

TABLE II
CALCULATIONS OF BOND ANGLE

| Assumed distances, Å | | | |
|----------------------|------|-------------------|------------------------------------|
| Atom distance | | Carboxylate group | Calculated value, angle Al—O—Al |
| Al—O | O—O | O—O | |
| 1.92 | 2.50 | 1.90* | 134° |
| | 2.71 | 1.83* | 130° |
| | 2.50 | 2.28 | 144° |
| | 2.71 | 2.28 | 140° |
| | | | 137° |

*Minimum distance of the bridge carboxylate O—O distance projected on the Al—O—Al plane as it oscillates from its average position.

It has been shown by Kuhn and others (16, Chap. X) that for polymer coils not extended by solvent-polymer interaction, the root-mean-square end-to-end distance could be related to the number and structure of the unit comprising the chain by the following relation,

$$r^2 = nl^2 [(1 + \cos \alpha) (1 + \cos \psi) / (1 - \cos \alpha) (1 - \cos \psi)], \quad [1]$$



where l is the unit length, i.e. the O—Al—O length; n , the number of units, $n = M_z/M_0$; α is the supplement of the valence angle Al—O—Al, i.e. $180^\circ - 135^\circ = 45^\circ$; and ψ the average value of the angle between the $(i+2)^{\text{th}}$ bond and the plane of the two preceding ones. All the units must be expressed in terms of the same average. The root-mean-square end-to-end distance $(\bar{r}^2)^{1/2}$ is derived from R_g —the radius of gyration—which as measured by light-scattering is a "Z" average value. The average number of units in the chain must also be a Z average, which means that the M in the equation must also be a Z average molecular weight. To calculate values of M_z it was assumed that the molecular weight distribution could be expressed by an exponential distribution function, especially since the molecular weight will be large (17).

$$M_n : M_w : M_z : k : k+1 : k+2 \quad [2]$$

Since the relation of M_w to M_n is given in Fig. 5, it is possible to find k , and M_z/M_n will be $(k+2)/(k+1)$. This ratio is given in Table III, together with the M_w molecular weight as derived by light-scattering measurement and from which M_z is obtained. This in turn gives n in equation [1].

The evaluation of the end-to-end distance by the relation given above [1] involves two basic steps. The first calculation—equivalent to a kinetic theory random-walk problem—gives the unit length of the polymer chains if no restriction whatsoever is imposed on the orientation of each link to its predecessor. The second, expressed in [1] as a ratio of the cosine of various angles, restricts this orientation for certain conditions imposed by steric hindrance, valency angles, and bond position. The unit length of the polymer chain without any angle restriction is about 26.3 Å, as given in Table III.

TABLE III
 BOND LENGTHS IN ALUMINUM DISTEARATE

| Molecular weight (W), Mw $\times 10^{-5}$ | Factor (k+2)/(k+1) | Molecular weight (Z), Mz $\times 10^{-5}$ | N = Mz/Mo $\times 10^{-4}$ | $(\bar{r}^2)^{1/2}$ Å | Unit length | |
|----------------------------------------------|-----------------------|----------------------------------------------|-------------------------------|-----------------------|---------------------------------------|-------------------------------------|
| | | | | | Uncorrected for chain angles, Å | Corrected for chain angles, Å |
| 25.8 | 1.98 | 51.1 | 8.42 | 6840 | 23.5 | 4.02 |
| 12.9 | 1.95 | 25.2 | 4.13 | 4920 | 24.2 | 4.14 |
| 11.5 | 1.94 | 22.3 | 3.66 | 4400 | 23.0 | 3.94 |
| 10.9 | 1.94 | 21.2 | 3.48 | 4200 | 22.5 | 3.85 |
| 9.10 | 1.93 | 17.6 | 2.88 | 4020 | 23.7 | 4.05 |
| 7.35 | 1.93 | 14.2 | 2.33 | 3690 | 24.2 | 4.14 |
| 6.50 | 1.92 | 15.5 | 2.05 | 3500 | 24.4 | 4.17 |
| 6.45 | 1.92 | 12.4 | 2.04 | 3730 | 26.2 | 4.48 |
| 5.72 | 1.91 | 10.90 | 1.79 | 3660 | 27.4 | 4.68 |
| 5.10 | 1.91 | 9.74 | 1.59 | 3320 | 26.4 | 4.52 |
| 3.96 | 1.90 | 7.52 | 1.23 | 3120 | 28.2 | 4.82 |
| 3.82 | 1.90 | 7.26 | 1.20 | 3030 | 27.6 | 4.72 |
| 3.74 | 1.90 | 7.10 | 1.16 | 2830 | 26.3 | 4.50 |
| 3.68 | 1.90 | 7.00 | 1.15 | 2910 | 27.2 | 4.65 |
| 3.39 | 1.89 | 6.43 | 1.05 | 2880 | 28.2 | 4.83 |
| 2.58 | 1.88 | 4.36 | 0.798 | 2500 | 28.0 | 4.79 |
| 2.34 | 1.87 | 4.42 | 0.726 | 2220 | 26.0 | 4.44 |
| 1.32 | 1.72 | 2.27 | 0.371 | 1840 | 30.2 | 5.16 |
| 1.25 | 1.58 | 1.98 | 0.324 | 1620 | 28.2 | 4.83 |
| Average | | | | | 4.46 | |

The magnitude of the correction factor to be applied to this value for steric hindrance and valency angle will depend on the choice of the angles α and ψ . It has been shown that since α is the supplement of the Al—O—Al angle, it has a value of 45° . It is more difficult to choose a value for ψ . It is defined as the angle between the $(i+2)^{\text{th}}$ bond and the plane made by the preceding two bonds, and is equivalent to a restriction or rotation about the bond axis. In the case of aluminum disoap, free rotation is stopped at either 0° or 90° by the bridge structure. The average value of ψ is then 45° , which is the value used in [1].

These give an average unit length of 4.46 Å, as found in Table III. The lower values are probably more accurate as the number of units are greater and statistically more probable. This O—Al—O length is of course $2(\text{Al—O})$, giving an Al—O bond length of 2.23 Å, compared with the calculated Al—O distance of 1.92 Å, as obtained from covalent radii.

Benoit (18) has shown that for polydisperse polymers made up of Gaussian chains, it is possible to obtain the number-average molecular weight and radius of gyration from the usual Zimm plot of the light-scattering data from the slope of the asymptote to the reciprocal scattering envelope at infinite dilution and at high-scattering angles. Unfortunately most of the data on aluminum stearate solutions were obtained with the dodecagonal cell, and extrapolation of this data is rather difficult with data available for only two backward angles. Several solutions were measured in a cylindrical cell with flat entrance and exit windows and the usual reflection and volume corrections made. Since the number-average molecular weight and root-mean-square end-to-end distance can both be calculated from the asymptote, no assumption need be made regarding the molecular weight distribution characteristics of the polymer. Three solutions examined in this way gave a number-average molecular weight of 2.48×10^5 , 2.90×10^5 , and 9.0×10^5 , with an $(\bar{r}_g^2)^{1/2}$ of 492 Å, 680 Å, and 835 Å, respectively. This leads to an

O—Al—O distance of 4.19 Å, 3.78 Å, and 3.80 Å, with the same equations and angle assumptions used previously. These bond length values are very close to those obtained by assuming a molecular weight distribution for the polymer and are a further indication of the validity of the assumptions made in the calculations.

E. Flory's Relationship

Flory (16) has postulated that for linear random coil molecules

$$[\eta] = \Phi(\bar{r}^2)^{3/2}/M$$

where $(\bar{r}^2)^{1/2}$ is the root-mean-square end-to-end distance of the molecule and Φ is a constant usually taken as 2.1×10^{21} .

In Fig. 9 this relationship is given as a function of M_w as determined by light-scattering. This relation has been shown to hold for various polymer systems of linear molecules. In the present case, there is a slight molecular weight dependence in Φ , probably because of the increasing polydispersity at higher molecular weights. The intercept gives the Φ value found for other systems namely 2.1×10^{21} .

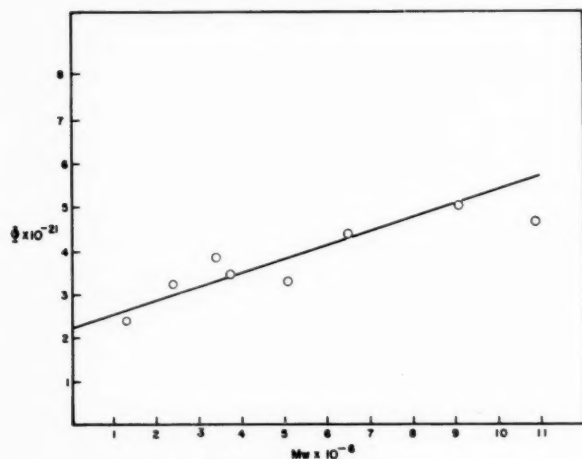


FIG. 9. Flory's Φ values as a function of weight-average molecular weight (M_w).

CONCLUSION

The results indicate that in dilute benzene solutions aluminum stearate is a linear molecule of random coil shape. In support of this conclusion, there is the expected intrinsic viscosity - molecular weight relationship, the experimental data satisfies the theoretical curves for random coils, the constancy of the ratio of the molecular weight to the square of the radius of gyration, the very close approximation of the Al—O bond length obtained by calculations based on this assumption, and expected value of Φ in the Flory intrinsic viscosity relationship.

It can also be concluded that for the aluminum distearate solutions, as prepared for our measurements, branching is not a predominant factor and the slight deviations from the usual linear molecules' behavior found above could be explained by the known very wide distribution of molecular weight.

ACKNOWLEDGMENTS

The authors wish to thank Dr. C. E. Hubley and Mr. R. L. Haines for helpful discussions and Mr. W. D. Barnes for technical assistance.

REFERENCES

1. GRAY, V. R. *Trans. Faraday Soc. B*, **42**, 196 (1946).
2. MCBAIN, J. W. and WORKING, E. B. *J. Phys. & Colloid Chem.* **51**, 974 (1947).
3. MCROBERTS, T. S. and SCHULMAN, J. H. *Nature*, **162**, 101 (1948).
4. SHEFFER, H. *Can. J. Research, B*, **26**, 481 (1948).
5. GRAY, V. R. and ALEXANDER, A. E. *J. Phys. & Colloid Chem.* **53**, 9, 23 (1949).
6. MCGEE, C. J. *J. Am. Chem. Soc.* **71**, 278 (1949).
7. SCOTT, F. A., GOLDENSON, J., WIBERLY, S. E., and BAUER, W. H. *J. Phys. Chem.* **58**, 61 (1954).
8. LEGER, A. E., HAINES, R. L., HUBLEY, C. E., HYDE, J. C., and SHEFFER, H. *Can. J. Chem.* **35**, 799 (1957).
9. HADOW, H. J., SHEFFER, H., and HYDE, J. C. *Can. J. Research, B*, **27**, 791 (1949).
10. SHEFFER, H. and HYDE, J. C. *Can. J. Chem.* **30**, 817 (1952).
11. STACEY, K. A. *Light-scattering in physical chemistry*. Butterworth Scientific Publications, London, 1956.
12. RICE, S. A. *J. Polymer Sci.* **16**, 94 (1955).
13. GOLDSTEIN, M. *J. Chem. Phys.* **21**, 1255 (1953).
14. PAULING, L. *The nature of the chemical bond*. 2nd ed. Cornell Univ. Press, Ithaca, N.Y. 1945.
15. AGGARWAL, E. H. and BAUER, S. H. *J. Chem. Phys.* **18**, 42 (1950).
16. FLORY, P. J. *Principles of polymer chemistry*. Cornell Univ. Press, Ithaca, N.Y. 1953.
17. BILLMEYER, F. W., JR. and STOCKMAYER, W. J. *J. Polymer Sci.* **5**, 121 (1950).
18. BENOIT, H., HOLTZER, A. M., and DOTY, P. *J. Phys. Chem.* **58**, 635 (1954).

NOTES

RESONANCE PARAMETERS FROM REACTIVITY CONSTANTS

C. N. RAMACHANDRA RAO* AND G. K. GOLDMAN

Recently, McDaniel and Brown (1) have compiled an extensive set of Hammett σ values based upon the ionization of benzoic acids. A number of electrophilic substituent constants, σ^+ , have also been calculated based on the thermodynamic dissociation constants of benzoic acids by Brown and Okamoto (2). The σ^+ constants differ from the σ constants by an extra resonance factor resulting from the greater opportunity for resonance interaction by the substituents in electrophilic reactions. Such strong resonance interactions in electrophilic reactions occur between the electron-donating substituents and the electron-deficient centers of the reacting systems. Accordingly the σ_p^+ values differ greatly from the σ_p values for the ortho-para-directing groups. But the σ and σ^+ constants for the meta-directing substituents are very similar and the deviations fall within the limit of the estimated uncertainties of the constants (3). This is understandable, since the meta-directing groups exhibit no significant resonance interaction with the incipient carbonium ion. As one would expect, the σ_m and σ_m^+ values for groups are also similar, since the major contribution of a meta-substituent is by inductive interaction.

Although the resonance parameters of the substituents should vary with the electronic demands of the reaction, it has been possible to propose a single set of σ^+ values which would correlate the available data on electrophilic aromatic substitution and electrophilic side-chain reactions with good precision (2, 4). This suggests that the σ^+ constants can also be separated to independent inductive and resonance contributions similar to the quantitative separation of the Hammett σ constants by Taft (5),

$$\sigma^+ = \sigma_I + \sigma_R^+,$$

where σ_I and σ_R^+ are the inductive and resonance parameters respectively. The inductive

TABLE I
RESONANCE PARAMETERS FROM σ AND σ^+ CONSTANTS

| | σ_I | $\sigma_R = \sigma_p - \sigma_I$ | $\sigma_m - \sigma_I$ | $\sigma_R^+ = \sigma_p^+ - \sigma_I$ | $\sigma_m^+ - \sigma_I$ |
|------------------------------------------------|------------|----------------------------------|-----------------------|--------------------------------------|-------------------------|
| NH ₂ | +0.10 | -0.76 | -0.26 | -1.40 | -0.26 |
| OH | +0.25 | -0.62 | -0.13 | -1.17 | — |
| OCH ₃ | +0.25 | -0.52 | -0.14 | -1.03 | -0.20 |
| F | +0.52 | -0.46 | -0.18 | -0.59 | -0.17 |
| SCH ₃ | +0.25 | -0.25 | -0.10 | -0.85 | -0.09 |
| Cl | +0.47 | -0.24 | -0.10 | -0.36 | -0.07 |
| NHCOCH ₃ | +0.28 | -0.28 | -0.07 | -0.88 | — |
| Br | +0.45 | -0.22 | -0.06 | -0.30 | -0.05 |
| (CH ₃) ₂ C | -0.07 | -0.13 | -0.03 | -0.19 | +0.01 |
| I | +0.39 | -0.21 | -0.04 | -0.26 | -0.03 |
| CH ₃ | -0.05 | -0.12 | -0.02 | -0.26 | -0.02 |
| C ₆ H ₅ | +0.10 | -0.11 | -0.04 | -0.28 | -0.01 |
| H | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| N(CH ₃) ₂ | +0.86 | -0.04 | +0.02 | -0.45 | -0.50 |
| CF ₃ | +0.41 | +0.13 | +0.02 | +0.20 | +0.11 |
| (CH ₃) ₂ Si | -0.12 | +0.05 | +0.08 | +0.14 | +0.13 |
| CN | +0.59 | +0.07 | -0.03 | +0.07 | -0.03 |
| C ₂ H ₅ O ₂ C | +0.32 | +0.13 | +0.05 | +0.16 | +0.05 |
| NO ₂ | +0.63 | +0.15 | +0.08 | +0.16 | +0.04 |

* Presently at the Department of Chemistry, University of California, Berkeley, Calif.

parameters in this equation are the same as those proposed by Taft (5, 6). This is reasonable, since the inductive effect should essentially be independent of the reaction.

We have now calculated the $\sigma_p - \sigma_I$, $\sigma_m - \sigma_I$, $\sigma_p^+ - \sigma_I$ and $\sigma_m^+ - \sigma_I$ for several substituents based on the recent compilations of the σ and σ^+ values (1, 2). The results are summarized in Table I. In Fig. 1 are plotted the $\sigma_p - \sigma_I$ versus the $\sigma_p^+ - \sigma_I$ for the electron-donating groups. With the exception of $N(Me)_3$, $NCOMe$, SMe , and F groups, all the other groups fall on a straight line. By least-square treatment the line can be represented by the equation:

$$\sigma_R^+ = 1.91\sigma_R - 0.03.$$

This linearity further confirms the suggestion that σ_R^+ of a group is essentially a constant to a first approximation and that σ_R^+ is not a very sensitive function of ρ (4).

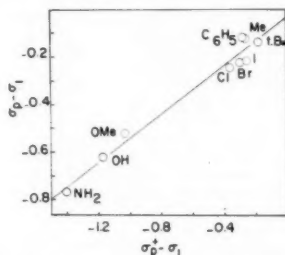


FIG. 1. Plot of σ_R^+ vs. σ_R for electron-donating groups.

ACKNOWLEDGMENT

The authors' thanks are due to Professor H. C. Brown for his kind interest.

1. McDANIEL, D. H. and BROWN, H. C. *J. Org. Chem.* **23**, 420 (1958).
2. BROWN, H. C. and OKAMOTO, Y. *In press*.
3. OKAMOTO, Y., INUKAI, T., and BROWN, H. C. *In press*.
4. OKAMOTO, Y. and BROWN, H. C. *J. Org. Chem.* **22**, 485 (1957).
5. TAFT, R. W. *In Steric effects in organic chemistry*. Edited by M. S. Newman, John Wiley & Sons, Inc., New York, 1956, Chap. 13.
6. TAFT, R. W. Technical Report No. 18. Office of Naval Research Contract No. 656(05), Project NRO55-328. Pennsylvania State University, 1958.

RECEIVED JULY 28, 1958.

RICHARD B. WETHERILL LABORATORY OF CHEMISTRY,
DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY,
LAFAYETTE, INDIANA, U.S.A.

REARRANGEMENT STUDIES WITH C^{14}

VI. THE FRIEDEL-CRAFTS ALKYLATION OF BENZENE WITH ETHYL- β - C^{14} IODIDE*

C. C. LEE, M. C. HAMBLIN, AND NADINE JAMES

In 1955, Roberts, Ropp, and Neville (1) reported that the Friedel-Crafts alkylation of benzene with ethyl- β - C^{14} chloride gave an ethylbenzene with no isotope position rearrangement in the ethyl side chain. When the ethyl- β - C^{14} chloride was allowed to stand over aluminum chloride at room temperature for 1 hour before being recovered and used to alkylate benzene, the ethylbenzene obtained showed rearrangements which

*Presented at the 41st Annual Conference of the Chemical Institute of Canada, Toronto, May 26-28, 1958.

indicated almost complete isomerization of the ethyl- β - C^{14} chloride by aluminum chloride. We have found substantially similar results for the alkylation of benzene with ethyl- β - C^{14} iodide, except that the aluminum chloride induced isomerization is much faster for the ethyl chloride (see Table I). Possibly, since chlorine is more electronegative than iodine, there may be a greater tendency for ethyl cation formation from ethyl chloride than from ethyl iodide under the influence of aluminum chloride.

TABLE I
REARRANGEMENTS IN THE FRIEDEL-CRAFTS ALKYLATION OF BENZENE WITH ETHYL- β - C^{14} IODIDE

| Expt. | Reaction conditions* | Compound counted | Corrected activity† | | % Rearrangement | |
|-------|---------------------------------------------------------------------|------------------|---------------------|---------------|-----------------|--------|
| | | | Run I | Run II | Run I | Run II |
| A | All reactants refluxed overnight | $C_6H_5C_2H_5$ | 7328 \pm 96 | 7152 \pm 96 | | |
| | | C_6H_5COOH | 20 \pm 6 | 25 \pm 6 | 0.3 | 0.3 |
| B | C_2H_5I and $AlCl_3$ stood at room temp. 1 hour before alkylation | $C_6H_5C_2H_5$ | 5040 \pm 70 | 5695 \pm 72 | | |
| | | C_6H_5COOH | 86 \pm 11 | 66 \pm 9 | 1.7 | 1.2 |
| C | C_2H_5I and $AlCl_3$ refluxed 1 hour before alkylation | $C_6H_5C_2H_5$ | 6912 \pm 85 | 5422 \pm 72 | | |
| | | C_6H_5COOH | 1448 \pm 19 | 1420 \pm 19 | 21 | 26 |

*The reactants used were 3.0 ml C_2H_5I , 1.5 g $AlCl_3$, and 60 ml C_6H_6 .

†Corrected activities in c.p.m. on a molar basis were determined by converting all compounds to barium carbonate and counted as infinitely thick samples of constant geometry in a gas flow Geiger counter. Correction for the dilution by non-labelled carbon atoms was made by multiplying the observed activity with the number of carbon atoms per molecule in the compound assayed.

The ethyl- β - C^{14} iodide was purchased from Atomic Energy of Canada Limited. The Friedel-Crafts reaction was carried out using 3.0 ml of labelled ethyl iodide, 1.5 g of anhydrous aluminum chloride, and 60 ml of redistilled benzene. The ethylbenzene obtained was oxidized with potassium permanganate to give benzoic acid, the radioactivity in which was taken as a measure of the rearrangement of the C^{14} -labelled atoms from the β - to the α -positions of the ethyl group. In Expts. B and C (Table I), the labelled ethyl iodide was treated with the aluminum chloride for 1 hour at room and reflux temperatures, respectively, before the resulting mixture was used to alkylate benzene. Similar yields of ethylbenzene, within the range of 70–75% of theoretical, were obtained in Expts. A, B, and C.

The degree of isotope position rearrangement induced by aluminum chloride on ethyl- β - C^{14} iodide is dependent on temperature as indicated by the results of Expts. B and C. It is also dependent on the length of the contact time of aluminum chloride with ethyl iodide. Mixtures of ethyl- β - C^{14} iodide (3.0 ml) and anhydrous aluminum chloride (1.5 g) were heated at 40° C for various lengths of time and the resulting material, without any fractionation, was used to alkylate an excess of benzene (60 ml). Isotope position rearrangements in the ethyl side chain of the ethylbenzene obtained are shown graphically in Fig. 1. Under these conditions, the degree of rearrangement was found to increase with length of contact time until a maximum of 50% rearrangement, corresponding to a complete equilibration of the α - and β -carbons of the ethyl group, is reached after about 42 hours.

The finding that aluminum chloride is capable of inducing isomerization in the labelled ethyl halide, while the ethylation of benzene under the usual Friedel-Crafts conditions yielded unrearranged ethylbenzene, was interpreted by Roberts, Ropp, and Neville (1) as meaning that the alkylation either follows a displacement mechanism involving no free ethyl fragments, or if a carbonium ion mechanism were operative, the ions react with the aromatic reactants so rapidly as to exclude internal hydride shifts. More recently,

Jungk, Smoot, and Brown (2) suggested that the Friedel-Crafts alkylation is another example of substitution on saturated carbon, which may have a continuum of mechanisms ranging between the extremes of a direct displacement and one involving an alkyl cation that could give rise to rearrangement. Still another possibility that rearrangement in the Friedel-Crafts alkylation may arise from a separate process which occurs before the product-forming alkylation step has been pointed out (3). Applying any one of these explanations to the present results, one would expect that the rate of the Friedel-Crafts reaction between ethyl iodide and benzene should be faster than the rate of the aluminum chloride induced rearrangement on ethyl- β -C¹⁴ iodide. It is thus of interest to measure the rate of the ethylation under our experimental conditions. Instead of the usual titration of the liberated hydrogen halide, we have estimated the rate of ethylbenzene formation by an isotope dilution technique. Since 1 mole of ethylbenzene is

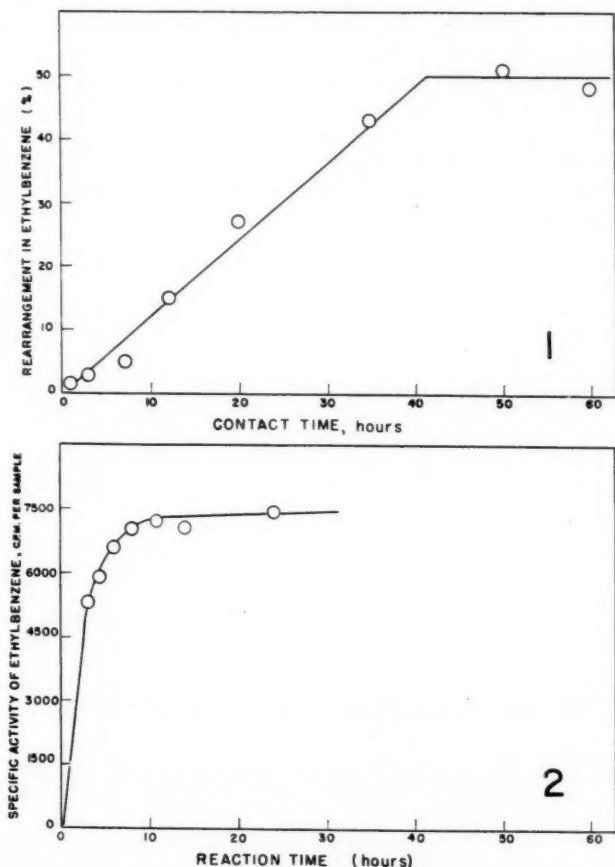


FIG. 1. Isotope position rearrangements in ethylbenzene from reaction of benzene with mixtures of labelled ethyl iodide and aluminum chloride that had been in contact at 40° for various lengths of time.

FIG. 2. Specific activities of ethylbenzene from aliquots of a Friedel-Crafts reaction at 40°, each aliquot having been diluted with a fixed amount of non-radioactive ethylbenzene.

produced from 1 mole of ethyl iodide, the activity per mole of the ethylbenzene formed should be the same as the activity per mole of the ethyl- β - C^{14} iodide used, though the total quantity of ethylbenzene produced would increase with reaction time. If aliquots of the reaction mixture were withdrawn at various time intervals and a fixed amount of non-labelled ethylbenzene added to each aliquot, the specific activity of the ethylbenzene samples recovered from these aliquots should increase with reaction time and would reach a constant maximum value after the reaction is complete. As the specific activity of the diluted ethylbenzene is a measure of the quantity of labelled ethylbenzene actually produced by the Friedel-Crafts reaction it is not necessary to have quantitative isolation of all ethylbenzene from each aliquot. The radiochemical purity of the recovered ethylbenzene can be rigorously established by showing that the specific activity of the diluted ethylbenzene from various aliquots does not change significantly on repeated distillation. Such a kinetic study was carried out at 40° C, the reactants initially present being 120 ml of benzene, 6.0 ml of ethyl- β - C^{14} iodide, and 3.0 g of aluminum chloride. The results are given graphically in Fig. 2, the plateau of constant maximum specific activity being reached in about 12 hours. Assuming the specific activity at the plateau of Fig. 2 corresponds to 100% reaction, it is possible to calculate the percentage of ethyl iodide remaining unreacted at various times before the reaction was complete. This is shown in a semilogarithmic plot in Fig. 3, indicating that the reaction, as expected, is first order with respect to ethyl iodide. The first-order specific rate constant derived from Fig. 3 is $0.81 \times 10^{-4} \text{ sec}^{-1}$.

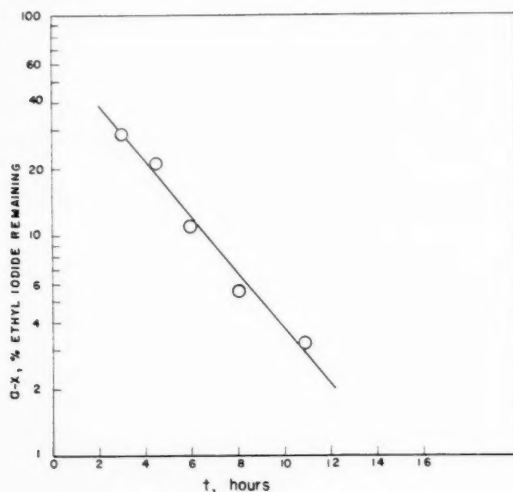


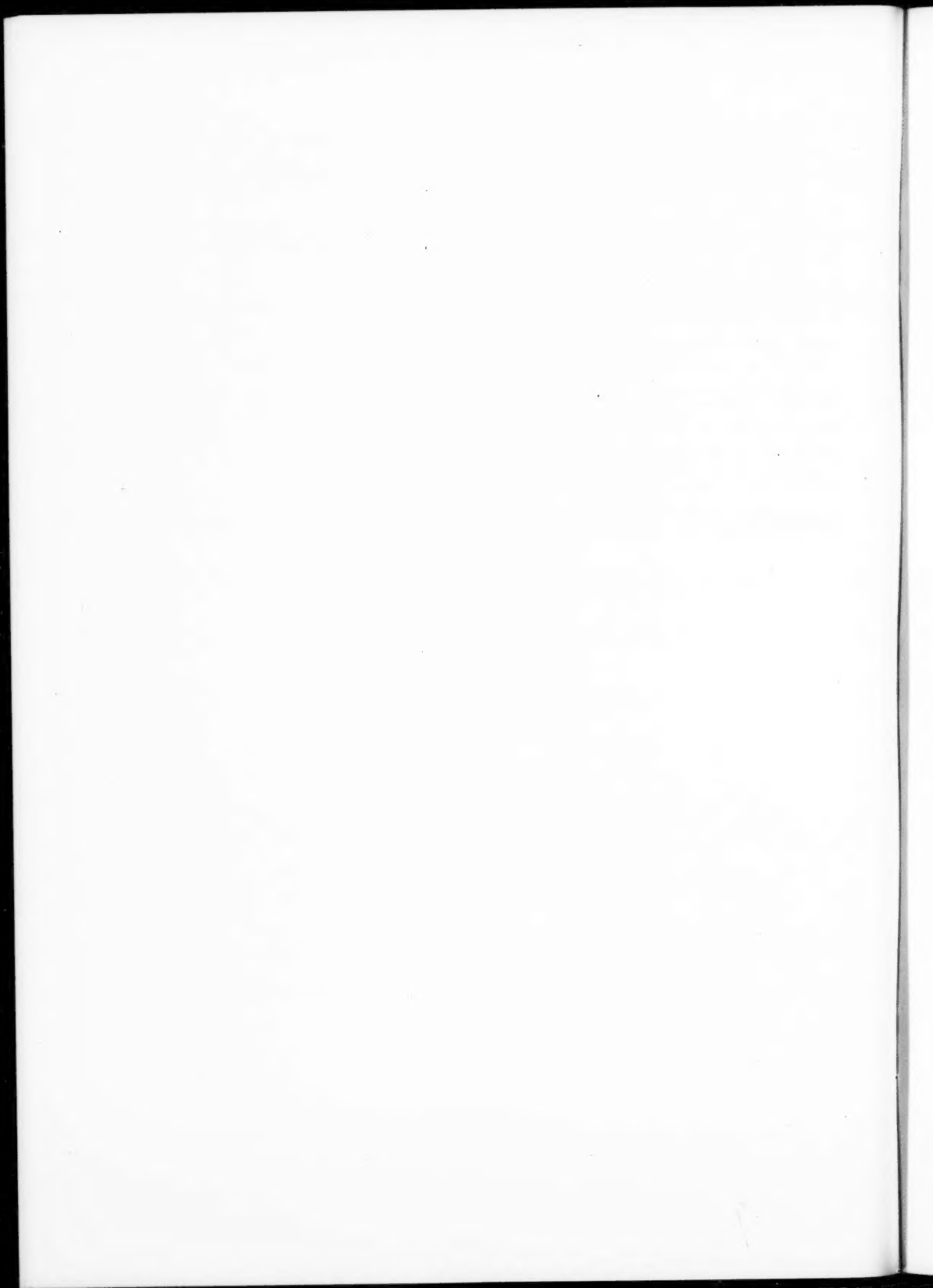
FIG. 3. First-order kinetic dependency on ethyl iodide in the formation of ethylbenzene. Calculated from Fig. 2.

Comparing Figs. 1 and 2, it is evident that at 40° C, the rate of the aluminum chloride induced rearrangement on pure ethyl iodide is slower than the rate of the Friedel-Crafts ethylation of benzene. Under the Friedel-Crafts reaction conditions, the ethyl iodide is diluted by the presence of an excess of benzene, thus the rate of the aluminum chloride induced rearrangement may be still slower. It is, therefore, reasonable to conclude that

in the Friedel-Crafts reaction between benzene and ethyl- β -C¹⁴ iodide, the rate of ethylbenzene formation is faster than the rate of a possible rearrangement of the ethyl iodide caused by the aluminum chloride.

1. ROBERTS, R. M., ROPP, G. A., and NEVILLE, O. K. J. Am. Chem. Soc. **77**, 1764 (1955).
2. JUNGK, H., SMOOT, C. R., and BROWN, H. C. J. Am. Chem. Soc. **78**, 2185 (1956).
3. LEE, C. C., FORMAN, A. G., and ROSENTHAL, A. Can. J. Chem. **35**, 220 (1957).

RECEIVED JUNE 24, 1958.
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SASKATCHEWAN,
SASKATOON, SASKATCHEWAN.



HELVETICA CHIMICA ACTA

SCHWEIZERISCHE
CHEMISCHE GESELLSCHAFT
Verlag Helvetica Chimica Acta
Basel 7 (Schweiz)

Seit 1918 **40**
Jahre

Abonnemente: Jahrgang 1958, Vol. XLI \$22.10 incl. Porto

**Es sind noch
lieferbar:**

Neudruck ab Lager
Vol. I–XIV (1918–1931)
Vol. XVII–XX (1934–1937)
Vol. XV, XVI, XXI–XXV (1932, 1933, 1936–1942) in Vor-
bereitung.
Originalausgaben, druckfrisch und antiquarisch.
Vol. XXVI–XL (1943–1957)
Diverse Einzelhefte ab Vol. XXI
Preise auf Anfrage. Nur solange Vorrat

Das wissenschaftliche Organ der

SCHWEIZERISCHEN
CHEMISCHEN
GESELLSCHAFT

Recueil des travaux chimiques des Pays-Bas

FONDÉ EN 1882 PAR

W. A. VAN DORP, A. P. N. FRANCHIMONT, S. HOOGEWERFF,
E. MULDER ET A. C. OUDEMANS

EDITED BY THE ROYAL NETHERLANDS CHEMICAL SOCIETY

Generally the "Recueil des travaux chimiques des Pays-Bas" only accepts papers for publication from members of the Royal Netherlands Chemical Society who are also subscribers to the Recueil. Applications for membership of this society should be sent to The Secretariate, Lange Voorhout 5, The Hague.

The Recueil contains papers written in English, French or German and appears if possible monthly (the 15th of each month) except in August and September, in issues of varying size. It is obtainable from D. B. Centen's Uitgeversmaatschappij, 1e Weteringplantsoen 8, Amsterdam, or through any bookseller in Holland or abroad. The subscription is 30.— guilders for Holland and 32.50 guilders abroad. Authors receive 75 reprints of their papers free of charge.

Editorial Office: Lange Voorhout 5, The Hague.



CANADIAN JOURNAL OF CHEMISTRY

Notes to Contributors

Manuscripts

(i) **General.** Manuscripts, in English or French, should be typewritten, double spaced, on paper $8\frac{1}{2} \times 11$ in. **The original and one copy are to be submitted.** Tables and captions for the figures should be placed at the end of the manuscript. Every sheet of the manuscript should be numbered.

Style, arrangement, spelling, and abbreviations should conform to the usage of recent numbers of this journal. Names of all simple compounds, rather than their formulas, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed.

Manuscripts and illustrations should be carefully checked before they are submitted. Authors will be charged for unnecessary deviations from the usual format and for changes made in the proof that are considered excessive or unnecessary.

(ii) **Abstract.** An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required, except in Notes.

(iii) **References.** These should be designated in the text by a key number and listed at the end of the paper, with the number, in the order in which they are cited. The form of the citations should be that used in this journal; in references to papers in periodicals, titles should not be given and only initial page numbers are required. The names of periodicals should be abbreviated in the form given in the most recent *List of Periodicals Abstracted by Chemical Abstracts*. All citations should be checked with the original articles and each one referred to in the text by the key number.

(iv) **Tables.** Tables should be numbered in roman numerals and each table referred to in the text. Titles should always be given but should be brief; column headings should be brief and descriptive matter in the tables confined to a minimum. Vertical rules should not be used. Numerous small tables should be avoided.

Illustrations

(i) **General.** All figures (including each figure of the plates) should be numbered consecutively from 1 up, in arabic figures, and each figure referred to in the text. The author's name, title of the paper, and figure number should be written in the lower left corner of the sheets on which the illustrations appear. Captions should not be written on the illustrations (see Manuscripts (i)).

(ii) **Line Drawings.** Drawings should be carefully made with India ink on white drawing paper, blue tracing paper, or co-ordinate paper ruled in blue only; any co-ordinate lines that are to appear in the reproduction should be ruled in black ink. Paper ruled in green, yellow, or red should not be used. All lines should be of sufficient thickness to reproduce well. Decimal points, periods, and stippled dots should be solid black circles large enough to be reduced if necessary. Letters and numerals should be neatly made, preferably with a stencil (**do NOT use typewriting**), and be of such size that the smallest lettering will not be less than 1 mm high when reproduced in a cut of suitable size.

Many drawings are made too large; originals should not be more than 2 or 3 times the size of the desired reproduction. Wherever possible two or more drawings should be grouped to reduce the number of cuts required. In such groups of drawings, or in large drawings, full use of the space available should be made; the ratio of height to width should conform to that of a journal page ($5\frac{1}{2} \times 7\frac{1}{4}$ in.) but allowance must be made for the captions.

The original drawings and one set of clear copies (e.g. small photographs) are to be submitted.

(iii) **Photographs.** Prints should be made on glossy paper, with strong contrasts. They should be trimmed so that essential features only are shown and mounted carefully, with rubber cement, on white cardboard, with no space between them. In mounting, full use of the space available should be made to reduce the number of cuts required (see Illustrations (ii)). Photographs or groups of photographs should not be more than 2 or 3 times the size of the desired reproduction.

Photographs are to be submitted in duplicate; if they are to be reproduced in groups one set should be mounted, the duplicate set unmounted.

Reprints

A total of 50 reprints of each paper, without covers, are supplied free. Additional reprints, with or without covers, may be purchased at the time of publication.

Charges for reprints are based on the number of printed pages, which may be calculated approximately by multiplying by 0.5 the number of manuscript pages (double-space typewritten sheets, $8\frac{1}{2} \times 11$ in.) and including the space occupied by illustrations. An additional charge is made for illustrations that appear as coated inserts. Prices and instructions for ordinary reprints are sent out with the galley proof.

Any reprints required in addition to those requested on the author's reprint requisition form must be ordered officially as soon as the paper has been accepted for publication.

Contents

| | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| <i>Ragini Anet</i> —Fused heterocyclics. Part II. Synthesis of quinolino-(2:3:3':2')-quinoline: an isomer of calycanline - - - - - | 1449 |
| <i>M. A. Weinberger, T. J. Mousseau, and O. Maass</i> —Electrolysis of lithium hydride - - - - - | 1455 |
| <i>Jacques Archambault and Roland Rivest</i> —Donor acceptor reactions of titanium tetrachloride with formamide and N,N-dimethyl formamide - - - - - | 1461 |
| <i>J. K. Gillham and T. E. Timell</i> —The hemicellulose of white elm (<i>Ulmus americana</i>). II. Constitution of the methyl glucurono-xylan - - - - - | 1467 |
| <i>A. N. Campbell, E. M. Kartzmark, and W. E. Falconer</i> —The system: nicotine - methylethyl ketone - water - - - - - | 1475 |
| <i>L. G. Stonhill</i> —The determination of UO_2 and U_2O_3 in brown oxide - - - - - | 1487 |
| <i>G. Giacometti and E. W. R. Steacie</i> —The gas phase reactions of perfluoro- <i>n</i> -propyl radicals with methane and ethane - - - - - | 1493 |
| <i>R. A. Abramovitch and J. R. Gear</i> —Unsymmetrically substituted 3,3'-methylene bridged 2,2'-dihydroxychromones - - - - - | 1501 |
| <i>A. N. Campbell, E. M. Kartzmark, and E. G. Lovering</i> —Reciprocal salt pairs, involving the cations Li , Na , and K , the anions SO_4 and Cl , and water, at 25° C - - - - - | 1511 |
| <i>P. J. Dyne and J. M. Kennedy</i> —The kinetics of radical reactions in the tracks of fast electrons. A detailed study of the Samuel-Magee model for the radiation chemistry of water - - - - - | 1518 |
| <i>Mary J. Chisholm and C. Y. Hopkins</i> —Fatty acids of the seed oil of <i>Cardiospermum halicacabum</i> - - - - - | 1537 |
| <i>R. A. B. Bannard, A. A. Casselman, W. F. Cockburn, and G. M. Brown</i> —Guanidine compounds. II. Preparation of mono- and N,N-di-alkyl-guanidines - - - - - | 1541 |
| <i>R. A. Heacock and (in part) M. E. Mahon</i> —The chemistry of the "aminochromes". Part II. The preparation, paper chromatography, and spectroscopic properties of pure adrenolutin: the infrared spectrum of adrenochrome - - - - - | 1550 |
| <i>Henry Sawatzky and George F. Wright</i> —The electrical polarizations of bis-mercurials - - - - - | 1555 |
| <i>E. Kerry Gill and Keith J. Laidler</i> —Theoretical aspects of the unimolecular decomposition of nitrous oxide - - - - - | 1570 |
| <i>Frederick J. Allan, G. Graham Allan, and J. B. Thomson</i> —The condensation of rhodanine with aromatic dialdehydes and some related compounds - - - - - | 1579 |
| <i>A. E. Leger, J. C. Hyde, and H. Sheffer</i> —Light-scattering studies on aluminum distearate - - - - - | 1584 |
| Notes: | |
| <i>C. N. Ramachandra Rao and G. K. Goldman</i> —Resonance parameters from reactivity constants - - - - - | 1596 |
| <i>C. C. Lee, M. C. Hamblin, and Nadine James</i> —Rearrangement studies with C^{14} . VI. The Friedel-Crafts alkylation of benzene with ethyl- β - C^{14} iodide - - - - - | 1597 |

